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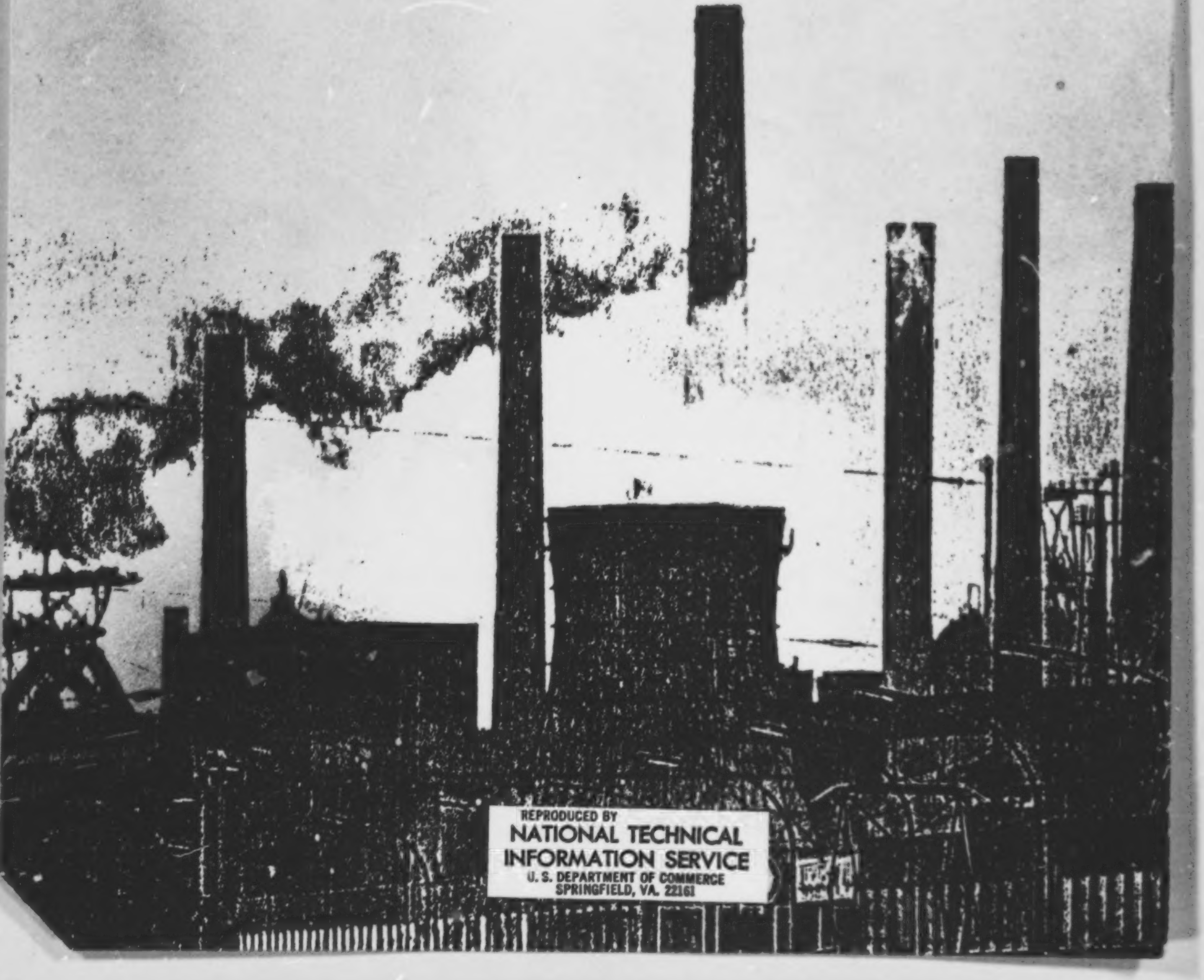
Volume 2
Characterization



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16. ABSTRACT

Technical papers on the characterization of primary sulfate emissions from combustion sources, presented at a workshop sponsored by the U.S. Environmental Protection Agency, are compiled in Volume 2 of a proceedings.

The objectives of the workshop were to review and discuss current measurement methods and problem areas for sulfur oxides emission with attention focused on sulfuric acid, sulfates, and sulfur-bearing particulate matter; to review and discuss emission data from various combustion sources operating under different conditions which include various pollutant controls, fuel composition, excess boiler oxygen, etc.; and to delineate and recommend areas in need of research and development effort.

Scientists were invited to present the result of their studies on primary sulfate emissions. The 3-day workshop devoted one day to measurement technology, a second to characterization, and a third to critical assessment of the presented papers and development of summary working group reports on each half-day session of the initial 2 days. Thirty-one papers were presented by 29 participants on measurements and characterization. Four working group reports were developed and summarized in the last day.

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In general, the technical content of the papers included in this report have been reproduced in the form submitted by the authors.

Any papers included in the Program and not included herein were not submitted for publication.

Preface

This volume contains the technical papers presented at the Workshop on Measurement Technology and Characterization of Primary Sulfur Oxides Emission from Combustion Sources held in Southern Pines, North Carolina, April 24-26, 1978. In addition, reports on deliberations and recommendations of four Working Groups (corresponding to the four sessions of technical presentations) are included.

A Working Group was formed for each of the four sessions of technical presentations and consisted of all the speakers of that session. Each Working Group met in a Working Group Session, reviewed and critiqued the session presentations, and made its initial report to all attendees in a summary session. The report summarized what is known and deemed acceptable and what further research activity needs to be pursued to provide desirable data and information. At the summary session, the initial report of each Working Group was discussed and further modified to reflect the comments and interaction between the Working Groups. The report of each Working Group resulting from this summary session is presented in this volume and follows the set of papers presented at the session it addresses.

The focus of sulfur pollutants impacting on ambient air quality has been the criteria pollutant, sulfur dioxide and its oxidation products, sulfuric acid and sulfate salts. Considerable attention has been directed to the sulfuric acid and sulfate salts resulting from the chemical transformation of SO_2 both temporally and spatially in the atmosphere. These are referred to as secondary sulfates. Sulfuric acid and sulfate salts emitted directly as emissions from combustion sources also impact on the ambient levels of sulfate.

These direct emissions of sulfuric acid and sulfate salts are referred to as primary sulfates.

Since sulfates at this time are not criteria pollutants and emission standards are not prescribed, no reference method is established for their measurement in combustion source emissions. With the current and ongoing concern about sulfur in fuels, there is increasing effort in measuring and characterizing sulfur-containing emissions from combustion sources. There is a need to identify valid measurement techniques for primary sulfates, specifically sulfuric acid, and to provide an accurate and consistent base of characterization data on primary sulfate emissions from the various combustion processes. There is also the need to determine what emission data on primary sulfates are available, their acceptability as valid measurements, and what further research effort needs to be conducted to provide a good data base for a good understanding of the contribution of primary sulfate emissions to ambient sulfate levels.

The purpose of this Workshop was to help meet these needs.

I am grateful for the active participation of the Workshop attendees who were invited to present and discuss their activities and studies in the area of primary sulfate emissions and for their contributions which made the Workshop an interesting and significant accomplishment. In particular, I want to thank the Session Chairmen (James Dorsey, Kenneth Knapp, James Homolya, and John Bachmann) and the Working Group Chairmen (Paul Urone, Dale Lundgren, James Howes, and David Natusch) for their assistance in implementing the Workshop agenda so effectively. I also want to include my appreciation for the efforts and cooperation of Ann Mitchell and Wendy Martin of Kappa Systems in coordinating the Workshop and in editing the Proceedings.

John S. Nader
Workshop Chairman

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Section 1

Gas Emissions

An Assessment of Sulfuric Acid and Sulfate Emissions from the Combustion of Fossil Fuels

James B. Homolya
James L. Cheney
U.S. Environmental Protection Agency

ABSTRACT

A series of studies were carried out in which stack gas emissions from both coal-fired and oil-fired sources were analyzed for sulfuric acid and total water-soluble sulfate. The sampling methods included: (1) a modified EPA Method 6 procedure for SO_2 and total water-soluble sulfate; (2) controlled-condensation procedure for sulfuric acid, sulfate, and SO_2; and (3) the determination of the sulfuric acid dewpoint temperature.

These methods were applied to the combustion emissions from industrial and utility-sized boilers. Our studies showed that for a given fuel sulfur content, the total sulfate emissions from oil-fired sources are from three to ten times greater than from sources burning coal. It is believed that the higher flame temperatures, the vanadium and nickel content, and the lack of particulate control devices for oil-firing contribute to the observed increases in emissions. In addition, a number of studies demonstrated that the available boiler oxygen in excess of stoichiometric will enhance sulfate formation.

Based on the work completed thus far, it appears that the free sulfuric acid content of the oil-fired source emissions is approximately 60% of the total sulfate level. The use of fireside fuel additives may alter the ratio of acid to sulfate. Through the use of dispersion models incorporating sulfate emission factors based upon

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our characterization studies, we found that the emission of primary sulfate species can have a marked impact on ambient sulfate concentrations downwind of combustion sources.

INTRODUCTION

A series of field sampling studies have been carried out to assess the atmospheric emissions of sulfates from coal-fired and oil-fired boilers. Emissions sources were selected which would be representative of a cross-section of boiler designs with respect to size, operating characteristics, and fuel usage. Flue gas samples were collected and analyzed for sulfur compounds by: (1) a modified EPA Method 6 procedure for SO_2 and total water-soluble sulfate; (2) a controlled-condensation procedure for sulfuric acid, sulfate, and SO_2; and (3) the determination of the sulfuric acid dewpoint temperature. Results obtained from studies over the past three years indicate a significantly higher level of sulfates in the flue gases of oil-fired boilers as compared to coal-fired sources. In general, the fraction of sulfur oxides emitted as sulfuric acid and/or sulfate has been found to be related to the metals content of the fuel as well as the amount of excess air used for combustion.

BACKGROUND

When characterizing the sulfur oxides emissions from combustion sources, one must be aware that several potential sulfate species can co-exist in the flue gases. Sulfuric acid can be found as: (1) a gas phase component at stack temperatures and water vapor concentrations; (2) a condensed liquid aerosol at temperatures below the acid dewpoint; and (3) adsorbed on carbonaceous particulate matter at stack gas temperatures. The latter component has been found to exist at temperatures in excess of 275°C (1). In addition, the free acid may react with metal oxides formed in the combustion flame to yield sulfates such as $Na_2(SO_4)$, $MgSO_4$, $VOSO_4$, and $Fe_2(SO_4)_3$ (2). For discussion we can identify sulfuric acid and its reaction products as being primary sulfate emissions and contrasted with sulfate (secondary sulfate) derived from the transformation of SO_2 in the atmosphere.

There are several factors which influence the nature and extent of primary sulfate emissions. These include: (1) fuel characteristics; (2) boiler design and operation; and (3) emissions controls. Coal-firing can be characterized as using a fuel which has a high ash content and is slow-burning. The principal metals found in coal are iron, silicon, and aluminum. Relatively low flame temperatures lessen the formation of H_2SO_4 by the combination of SO_2 with atomic oxygen in the flame (3), and the high ash content entrained in the flue gases tends to neutralize acid that is formed (4)(5). In contrast, oil is a fast-burning fuel with a low ash content. Principal metals found in fuel oils include vanadium, nickel, and sodium. An SO_2- atomic oxygen reaction may be enhanced by the higher oil-flame temperatures, and the effects of vanadium oxides on sulfate formation have been studied in residual oil-fired boilers (6). Therefore, for a given fuel sulfur content, one might expect that flue gases leaving an oil-fired unit may contain elevated levels of primary sulfate with respect to a coal-fired boiler of comparable size. Also the differences in fuel ash content (15% for coal versus 0.1% for oil) may reflect a large fraction of the primary sulfate emitted as free H_2SO_4 from oil-firing.

The extent of sulfate emissions can be affected by several boiler design parameters, including the number and type of burners, residence time and temperature distribution, and the amount of internal surface area. For a given boiler design, the boiler oxygen level in excess of stoichiometric has been found to be a significant factor in the formation of primary sulfates (7). Excess oxygen appears to enhance the catalytic action of deposits on metal surfaces. Therefore, the frequency and duration of sootblowing, as well as operating conditions which alter the residence time and temperature distribution in the unit, can influence the sulfate content of the flue gases.

With few exceptions, oil-fired sources are not equipped with any emissions controls. In the late 1960's many existing sources switched from coal to oil as a means of compliance with emissions regulations on sulfur dioxide and particulate matter. At the time most sources were using only mechanical particulate collectors which are ineffective for removing any significant quantity of ash from oil-firing. Coal-fired units are now equipped with electrostatic precipitators, and limited experiments have shown that their use can reduce sulfate emissions in excess of 50% (7). Within the last ten years most of the larger oil-fired boilers are burning a fuel containing corrosion inhibitors. These additions, usually containing MgO, are thought to either scavenge the vanadium oxides to form non-catalytic species or react with SO_3 to form a low melting ash which would not deposit in the high temperature sections of the boiler. The ash would then be retained in the flue gases to either deposit in an electrostatic precipitator or to be emitted to the atmosphere.

Primary Sulfate Emissions Characterization Studies

Since many independent factors were thought to influence the formation of primary sulfate, emissions characterization studies have been carried out on a large number of various sources encompassing a cross-section of boiler sizes, designs, and emissions controls. The SO_2 and primary sulfate levels were characterized for all sources using a modified EPA Method 6 procedure (8). In addition, as our measurement capability expanded, the components of the primary sulfate emissions were identified using a sulfuric acid dewpoint measurement (9) as well as a controlled-condensation method (10).

Summaries of emissions characterization studies for oil-fired and coal-fired units appear in Tables 1 and 2, respectively. Sources are identified with respect to their fuel sulfur and vanadium contents. The boiler excess oxygen is given and is identified as the flue gas oxygen level at the air heater inlet for large boilers and the stack gas oxygen content for packaged boilers not equipped with air heaters. The far right column expresses the total primary sulfate emissions as a weight percentage of the total sulfur oxides. In Table 1, Sources 2, 4, 6, 7, and 10 are industrial-sized units with the remainder being utility boilers. In general, industrial-sized boilers operate with higher excess oxygen levels and appear to emit a larger proportion of primary sulfate as compared to utility boilers burning oil of a similar sulfur content. Source 11 was the only oil-fired unit studied which was equipped with an electrostatic precipitator. The precipitator appears to reduce the sulfate emission by a factor of two. Source 12 is identical with Source 11 with the exception of not having a precipitator. The combined impact of low excess oxygen and fuel vanadium content was studied in detail at Source 15. For a given fuel vanadium content, increasing oxygen resulted in a measured increase in sulfate emissions. In addition, the highest primary sulfate emissions occurred with fuel containing the highest concentration of vanadium.

In Table 2, Source 1 is an industrial-sized unit. Coal is found to contain appreciably less vanadium than residual oil, and its combustion characteristics require higher excess air levels with respect to oil. However, the extent of primary sulfate emissions was found to be less than that from the combustion of oil of a similar sulfur content. In comparing the average of all the characterization measurements, the oil-fired sources emitted about 6.5 wt. % of the sulfur oxides as primary sulfate as compared to 2.1 wt. % of the sulfur oxides for coal.

Table 1. Summary of SO_2 and $SO_4^=$ Emission Measurements from Combustion Sources

Source	Sulfur wt. %	Vanadium, ppm by wt.	Boiler Excess O_2, %	$\frac{SO_4^=}{SO_2 + SO_4}$ = x 100, wt. %
A. Oil				
1. LILCO Barrett-#20	0.3%	50 ppm	1.8%	7%
2. EPA/Beaunit	0.2	<1	0	11
3. Ponce-South Coast #6	1.0	80	3	12
4. IBM-RTP	1.0	70	6	9
5. MICHOUD	1.2	16	3* -6	3-5
6. Burlington Industries-Durham	1.2	190	3	5
7. NCSU-Trane (HC1-HC4)	1.5	200	5	7
8. Albany-Unit #1	1.8	135	2.5	4
9. Albany-Unit #2	1.8	135	2.5	5
10. NCSU-Riley	2.0	375	5	8 at air heater inlet 10 at air heater outlet
11. LILCO-Northport #3	2.2	500	1.8	4 at air heater inlet 2 at precip. outlet
12. LILCO-Northport #2	2.2	500	1.9	5
13. Arthur M. Williams	2.2	447	2	7
14. San Juan-Palo Seco #1	2.5	300	1.2	4
15. Anclote I	2.5	140	0.3* -1.0	4-9
Anclote II	2.4	593	0.2* -0.6	6-12
Anclote III	2.6	292	0.1* -0.5	2-7 at air heater inlet 2-6 at air heater outlet

Table 2. Summary of SO_2 and $SO_4^=$ Emission Measurements from Combustion Sources

Source	Sulfur wt. %	Vanadium, ppm by wt.	Boiler Excess O_2, %	$\frac{SO_4^=}{SO_2 + SO_4}$ = x 100, wt. %
B. Coal				
1. UNC	1.7	<15	7	2.6
2. Wilmington	1.7	<15	4	1.4
3. KCP&L Hawthorne	1.7	<24	6	2.6
4. CPL - River Bend	1.9	39	5	0.9
5. CPL - Cape Fear	2.0	28	4	1.3
6. LG&E Mill Creek	3.6	99	4	3.5
7. CSO - Picway	3.3	35	5	2.8

We have analyzed the combustion particulate from coal-firing and oil-firing and find that oil ash characteristically contains about 30 wt. % sulfate and retains condensed sulfuric acid (11). Table 3 is a comparison of sulfate emissions data for two oil-fired sources with differing fuel sulfur and flue gas oxygen levels. Total sulfate was measured by the modified Method 6 procedure, and an acid dewpoint probe was used in combination with moisture determinations to provide a calculated free H_2SO_4 level. The source with the lowest flue gas oxygen level yielded the lowest primary sulfate concentration of which 28.1% consisted of H_2SO_4. In contrast, the source with 3% oxygen in the flue gas produced a higher sulfate level containing 54.8% H_2SO_4. By subtracting out the acid component of the total sulfate, it appears that the particulate sulfate content of both sources is nearly identical.

Primary Sulfate Emissions Impact on Ambient Air Environment

Based upon the results of characterization studies over the past few years, we have concluded that there is a significant difference in the emissions of primary sulfate between coal-fired and oil-fired combustion sources. Measurements have indicated that for a given fuel sulfur content, the total sulfate emissions from oil-fired sources are from three to ten times greater than from sources burning coal and contain a large fraction of free H_2SO_4. Residual oils are used in large quantities for both utility and industrial purposes in the Northeast sector of the U.S. where elevated ambient sulfate levels have been measured. The use of oil for electric generation has doubled over the last ten years. In 1967, oil accounted for about 9% of the energy generated as compared with 19% for 1977 (12). Much of this production occurs in urban centers where oil-firing is used to maintain ambient air total suspended particulate levels and SO_2 standards. Therefore, primary sulfates may prove to have a significant impact on ambient levels in regions of high emissions densities and where oil is the principal fuel.

Table 3. Comparison of Sulfate Emissions Data

	Palo Seco - Unit 1	South Coast - Unit 6
1. Fuel Sulfur	2.37%	0.99%
2. Flue Gas O_2, average, dry	1.28%	3.13%
3. Total SO_4^{-2}, average at Measured Flue Gas O_2, dry	1.28×10^5 $\mu g/m^3$	1.80×10^5 $\mu g/m^3$
4. Free H_2SO_4, average at Measured Flue Gas O_2, dry	0.36×10^5 $\mu g/m^3$	0.99×10^5 $\mu g/m^3$
5. South Coast total SO_4^{-2}, average at 1.28% O_2, dry	NA	1.97×10^5 $\mu g/m^3$
6. South Coast Free H_2SO_4, average at 1.28% O_2, dry	NA	1.08×10^5 $\mu g/m^3$
7. $\frac{H_2SO_4}{SO_4^{-2}}$ x 100, %	28.1%	54.8%
8. (Total SO_4^{-2} - Free H_2SO_4), at 1.28% O_2, dry	0.92×10^5 $\mu g/m^3$	0.89×10^5 $\mu g/m^3$

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Sulfur Oxides Emissions from Boilers, Turbines, and Industrial Combustion Equipment

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ABSTRACT

Measurements of sulfur oxides emissions were made on a wide variety of combustion devices, including boilers, gas turbines, and industrial process combustion equipment burning a variety of fuels.

Methods of measurement included continuous monitoring of sulfur dioxide and wet chemistry measurement of sulfur dioxide, sulfur trioxide, and sulfates using the Southern California air quality management district method, the Shell Emeryville method, and the Goksoyr-Ross method. Results from these measurements will be compared.

Emissions of sulfur trioxide from utility and industrial boilers are typically observed to vary from 1% to 6% of total sulfur oxides. Uncertainties in measurement methods producing high apparent levels of sulfur trioxide at low total sulfur oxide levels will be discussed.

Sulfur trioxide formation by means of gas phase kinetics, exclusive of surface catalytic action, was analzyed and levels typically observed were attributed to combustion of carbon monoxide in post-flame zones.

Sulfur retention in the ash from western coals will be compared with eastern coals fired in industrial boilers.

A limited amount of data will be presented on the effect of combustion modifications performed on an industrial boiler, and on the emissions of sulfur trioxide and sulfates.

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INTRODUCTION

This paper presents an evaluation of the formation of sulfur oxides in combustion equipment. Sulfur oxides emission is currently under regulation by air quality control authorities. Utility plant cold-end corrosion and emission of acid stack plumes have been identified as sulfur-related problems. Limited availability of low sulfur fuels demands that full attention be given to all possible means for controlling these emissions through plant operating procedures. The purpose of this paper is to examine the processes involved in sulfur oxide formation, review experience with test methods, and present test results for sulfur oxides emissions.

Thermodynamic equilibrium computations show that for practical fuel/air mixture ratios, the predominant sulfur species present in combustion gases are sulfur dioxide (SO_2) and sulfur trioxide (SO_3). At temperatures greater than 2500°F (1640 K), more than 99% of the sulfur is present as SO_2. At lower temperatures equilibrium shifts to increasing amounts of SO_3, so that below 700°F (644 K), more than 99% of the sulfur can be present in the form of SO_3. Limitations in the chemical kinetic rates, however, are such that only from 1% to 5% of the sulfur in stack gases is observed in practice to be present as SO_3 with the balance as SO_2.

Formation of SO_2 occurs early in the primary flame at rates comparable to the other combustion reactions. Formation will occur even in fairly fuel-rich flames so that no practical combustion control techniques have been identified. The only means for limitation of SO_2 emission is through control of the fuel sulfur content or by stack gas treatment.

Formation of SO_3 is found to occur only in air-rich mixtures and to be governed by kinetic processes more amenable to combustion control. Kinetic processes within the primary flame were found to be sufficiently fast so that SO_3 concentrations quickly approach equilibrium levels of less than 0.1% of the total sulfur. However, when combustion gases are cooled, a critical temperature region between 1500° and 3000°F (1090 and 1920 K) was found within which SO_3 is formed by gas phase kinetics, exclusive of any catalytic activity. Within this temperature range SO_2 can react with O atoms to form SO_3. At the low end of this temperature range formation ceases, and kinetic computations yield SO_3 concentrations between 1%-5% of total sulfur as observed in practice for excess oxygen levels greater than 1%.

Kinetic computations confirm that SO_3 can be reduced by lowering excess oxygen and suggest that the use of fuel-rich combustion, together with properly staged excess air addition, might be an effective method for SO_3 control. These same techniques have proved effective in control of oxides of nitrogen.

GAS PHASE KINETICS OF SULFUR OXIDES FORMATION

Thermodynamic Equilibrium Considerations

The thermodynamic equilibrium of burned mixtures containing sulfur indicates that the predominant sulfur compound is sulfur dioxide (SO_2). In air-rich mixtures a portion of the sulfur can be present as sulfur trioxide (SO_3). The amount of SO_3 expressed as a percent by volume of the total sulfur is a function of the mixture temperature and oxygen content. Figure 1 presents this relationship. At high temperatures, as in a flame, the amount of SO_3 is less than 0.1%. As temperature decreases, the relative amount of SO_3 increases to 100% at about 750°F (672 K). A critical temperature zone exists between 1000° and 2000°F (810 and 1370 K) where percent SO_3 changes rapidly. The fact that complete conversion of SO_3 does not occur in combustion units can only be explained by the rates at which the pertinent chemical reactions proceed. Consideration of the kinetic processes is therefore important in defining means for limiting SO_3 formation.

The figure also illustrates that the theoretical percent SO_3 is a function of the square root of the oxygen content. The very high level of theoretical percent SO_3 suggests that any form of catalytic activity in the cold regions of a power plant could result in very substantial levels of SO_3.

Gas Phase Kinetic Considerations

A review of measurements in flames, together with computations obtained with the use of computer programs developed by KVB, has resulted in an improved understanding of sulfur oxides formation processes.

Flame profile studies show that SO_2 formation occurs within the primary flame zone at rates comparable to other combustion reactions. Formation will proceed in both air-rich and fuel-rich flames at fuel-air ratios up to about 1.4 times stoichiometric. Formation of SO_2 is, therefore, unavoidable, and most of the fuel sulfur will be exhausted in this form. The only practical means for limiting SO_2 stack emission is through control of fuel sulfur

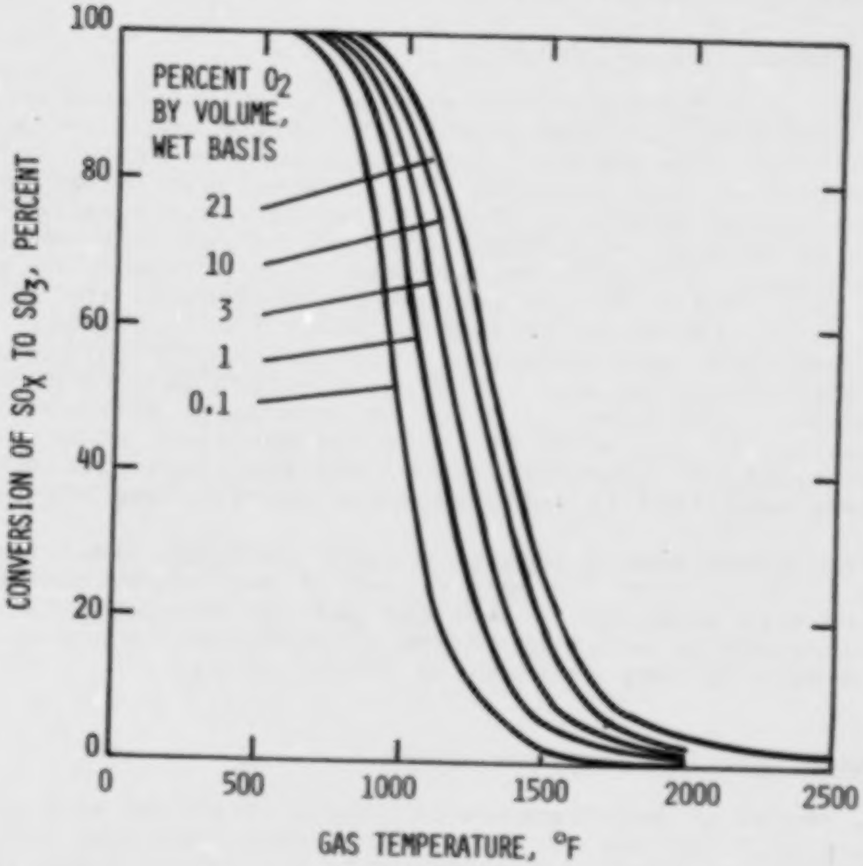

Figure 1. Thermodynamic equilibrium SO_3 conversion.

content or stack gas treatment. There are exceptions to complete sulfur emissions. These include ash retention of sulfur for certain coals and process materials absorption, as has been observed in cement kilns.

Several possible reactions forming SO_3 were defined; reaction of SO_2 with O atoms and a third body was identified as the most probable mechanism. Kinetic rate constants were obtained from the literature, and SO_2-SO_3 reactions, together with other reactions important in combustion, were evaluated with the KVB one-dimensional chemical kinetic computer program. Calculations were performed to examine the primary flame zone and the effects of post flame cooling and mixing of excess air.

Adiabatic flame zone computations indicated that peaks of SO_3 can occur that coincide with peaks of O atom concentration resulting from CO combustion. However, as the combustion reactions reach equilibrium, SO_3 concentrations drop to less than 1 ppm, so that the adiabatic flame zone does not appear to be a significant source of SO_3.

As post flame gases are cooled, O atom concentrations exceed equilibrium, and SO_3 begins to increase at about 3000°F (1922 K). As temperature drops to the range of 1500° to 2000°F (1090 to 1400 K), O atom production ceases. SO_3 concentration dictated by equilibrium now exceeds actual concentrations, but O atoms are rapidly depleted preventing further SO_3 increase. SO_3 formation ceases and concentration remains constant with further cooling. The final level of SO_3 is found to be dependent on O_2 content, rate of cooling, and rate and location of excess air mixing. The effects are critical primarily in a temperature range of 1500° to 3000°F (1090 to 1920 K). Fuel-rich combustion does not result in any SO_3 formation, and the use of fuel-rich combustion, together with staged air addition and reduced excess oxygen, appears to be a possible method of SO_3 control. Control of heat transfer in various sections of the plant, although difficult to implement, is also suggested as a possible reduction technique.

The results of kinetic analysis described below in general indicate that gas phase reactions can explain the observed levels of SO_3 independent of any catalytic surface activity. Undoubtedly both mechanisms contribute to SO_3 formation.

Formation of SO_3 in the Adiabatic Flame Zone--Sulfur trioxide (SO_3) can be formed by several reactions. Cullis (1) and Merryman (2) present discussions of the possible and most probable formation processes. The various reactions considered include:

$$SO_2 + O + M \rightleftarrows SO_3 + M \qquad [1]$$

$$SO_3 + O \rightleftarrows SO_2 + O_2 \qquad [2]$$

$$SO_2 + O \rightleftarrows SO_3 \qquad [3]$$

$$SO_3 + H \rightleftarrows SO_2 + OH \qquad [4]$$

$$SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3 \qquad [5]$$

$$SO + O_2 + M \rightleftarrows SO_3 + M \qquad [6]$$

$$SO_3 + H_2 \rightleftarrows SO_2 + H_2O \qquad [7]$$

$$SO_2 + NO_2 \rightleftarrows SO_3 + NO \qquad [8]$$

$$SO_2 + HO_2 \rightleftarrows SO_3 + OH \qquad [9]$$

Reactions involving direct O_2 attack on SO_2 have been shown to be very slow (1)(3). Significant rates of flame-produced SO_3 are only observed in the presence of O atoms and can be attributed to reactions [1] and [3]. Merryman (2) showed that SO_3 formation is strongly pressure dependent and concluded that the third body reaction [1] is the predominant reaction. This conclusion is supported by many others as discussed by Cullis (1). Reaction [1] is opposed by reaction [2] which acts to reconvert SO_3 back to SO_2. Sawyer (4) suggests that reaction [9] may be important in low temperature regions.

Thermodynamic equilibrium considerations indicate that at flame temperatures the percent SO_2 converted to SO_3 is less than 0.1%. However, this also implies that all other species are in equilibrium, particularly the O atoms. This is clearly not the case in the flame zone. When one species, in particular CO, has a slower rate of reaction, the remaining much faster reactions assume a different equilibrium. In particular, O atoms increase by factors of 10 to 1000 times the value established by O-O_2 equilibrium. The driving force for reaction [1] then establishes a different single-reaction equilibrium for the ratio of SO_3 to SO_2 concentration, so that the mole fraction of SO_3 can be increased over the complete equilibrium levels in proportion to the increase in O atom concentration above complete equilibrium levels. Inclusion of reaction [2] in this consideration indicates that the SO_3-SO_2 ratio would tend to stabilize at a value intermediate between the equilibrium value and the upper limit determined by excess O atom concentration. As the main combustion reactions reach completion, the O atom concentration returns to equilibrium with O_2, and flame-produced SO_3 can be reconverted to SO_2 by the reverse of reaction [1] and by reaction [2]. The combined effects of reaction [1] and [2] are such that a peak in SO_3 is observed in flame profiles as reported by Levy (2)(3)(5)(6)(7) and Hedley (8). The relative rates of these reactions must be considered to determine whether there is a possibility that the high flame SO_3 levels could persist beyond the flame by quenching of the reaction rates through cooling or mixing.

Computations have been performed to investigate the SO_3 formation process in the flame region employing a one-dimensional gas phase kinetics program developed by KVB. A fuel oil with basic composition of C_nH_{2n} plus 1% sulfur was used. The flame profile measurements previously discussed have shown that SO_3 formation occurs beyond the region of H_2 combustion and within the region of CO combustion. Accordingly, kinetic computations were initiated as a mixture of CO and H_2O and radical concentrations determined from equilibrium computations with formation of CO_2 and SO_3 suppressed. The sulfur was introduced entirely as SO_2.

The kinetic mechanism employed, presented in Table 1, is taken from that of Breen, Bell, and Bayard de Volo (9) with the addition of reactions [1] and [2] and updated rate constants for more recent values.

Kinetic calculations were performed at a constant pressure of one atmosphere for adiabatic combustion with air preheated to 450°F (506 K) to determine SO_3 concentrations as a function of time. The fuel to air ratio was varied from 0.87 to 1.3 times the stoichiometric fuel-air ratio to simulate the range of burner operation from lean at 3% O_2 to fuel-rich. Figure 2 presents the gas temperature and SO_3 concentration profiles as a function of time. The temperature increases monotonically from that for partial combustion only to CO and H_2O up to the adiabatic flame temperature. SO_3 is observed to rise to a peak and fall rapidly back to near equilibrium values within less than 0.001 second. The peak SO_3 level varies from 12 ppm at 3% O_2 to 2 ppm for fuel-rich combustion and is obviously a strong function of O_2 content. A level of 1% sulfur in the fuel produces SO_3 concentrations of from 480 ppm to 680 ppm in the flame region. Five ppm of SO_3, then, corresponds to approximately 1% conversion of sulfur to SO_3, so that observed peak SO_3 levels vary from 0.3% in fuel-rich flames

Table 1. Reaction Set for Combustion with Sulfur

REACTIONS	BACKWARD RATE CONSTANTS	REFERENCE
Third Body Reactions		
$SO_3 = SO_2 + O$	A = 1.00E15, N = 0.0, B = 0.0	[1]
$N_2 = N + N$	A = 1.E18, N = 1.0, B = 0.0	[9]
$O_2 = O + O$	A = 1.9318, N = 0.5, B = 0.0	[9]
$H_2 = H + H$	A = 7.5E18, N = 1.0, B = 0.0	[9]
$OH = O + H$	A = 3.6E18, N = 1.0, B = 0.0	[9]
$H_2O = OH + H$	A = 1.17E17, N = 0.0, B = 0.0	[10]
$CO_2 = CO + O$	A = 5.1E15, N = 0.0, B = 3.58	[9]
$NO_2 = N + O$	A = 1.0E20, N = 1.5, B = 0.0	[11]
$NO_2 = O + NO$	A = 1.05E15, N = 0.0, B = -1.87	[10]
$N_2O = O + N_2$	A = 1.00E18, N = 1.0, B = 0.0	[9]
CO/CO_2 Reactions		
$CO_2 + H = CO + OH$	A = 5.6E11, N = 0.0, B = 1.08	[10]
$CO + O_2 = CO_2 + O$	A = 1.9E13, N = 0.0, B = 54.15	[9]
H_2/O_2 Reactions		
$OH + H = H_2 + O$	A = 1.74E13, N = 0.0, B = 9.45	[10]
$H_2O + H = OH + H_2$	A = 2.19E13, N = 0.0, B = 5.15	[10]
$OH + O = H + O_2$	A = 2.24E14, N = 0.0, B = 16.8	[10]
$H_2O + O = OH + OH$	A = 5.75E12, N = 0.0, B = 0.78	[10]
Nitrogen Reactions		
$NO + O = O_2 + N$	A = 6.43E9, N = -1.0, B = 6.250	[10]
$N_2 + O = NO + N$	A = 3.10E13, N = 0.0, B = 0.334	[10]
$NO + H = OH + N$	A = 4.20E13, N = 0.0, B = 0.9	[12]
$NO + O_2 = NO + O$	A = 1.00E13, N = 0.0, B = 0.600	[10]
$N_2 + O = N_2O + O$	A = 3.00E13, N = 0.0, B = 26.8	[9]
Sulfur Reactions		
$SO_2 + O_2 = SO_3 + O$	A = 1.20E12, N = 0.0, B = 9.5	[1]

$k = A\ T^{-N} e^{(B/RT)}$

$R = 0.001987$ kcal/mole-°K

B in kcal/mole

T = temperature, °K

k = rate constant, $(cm^3/mole)^n sec^{-1}$

n = 1 for biomolecular reactions
  = 2 for third body reactions

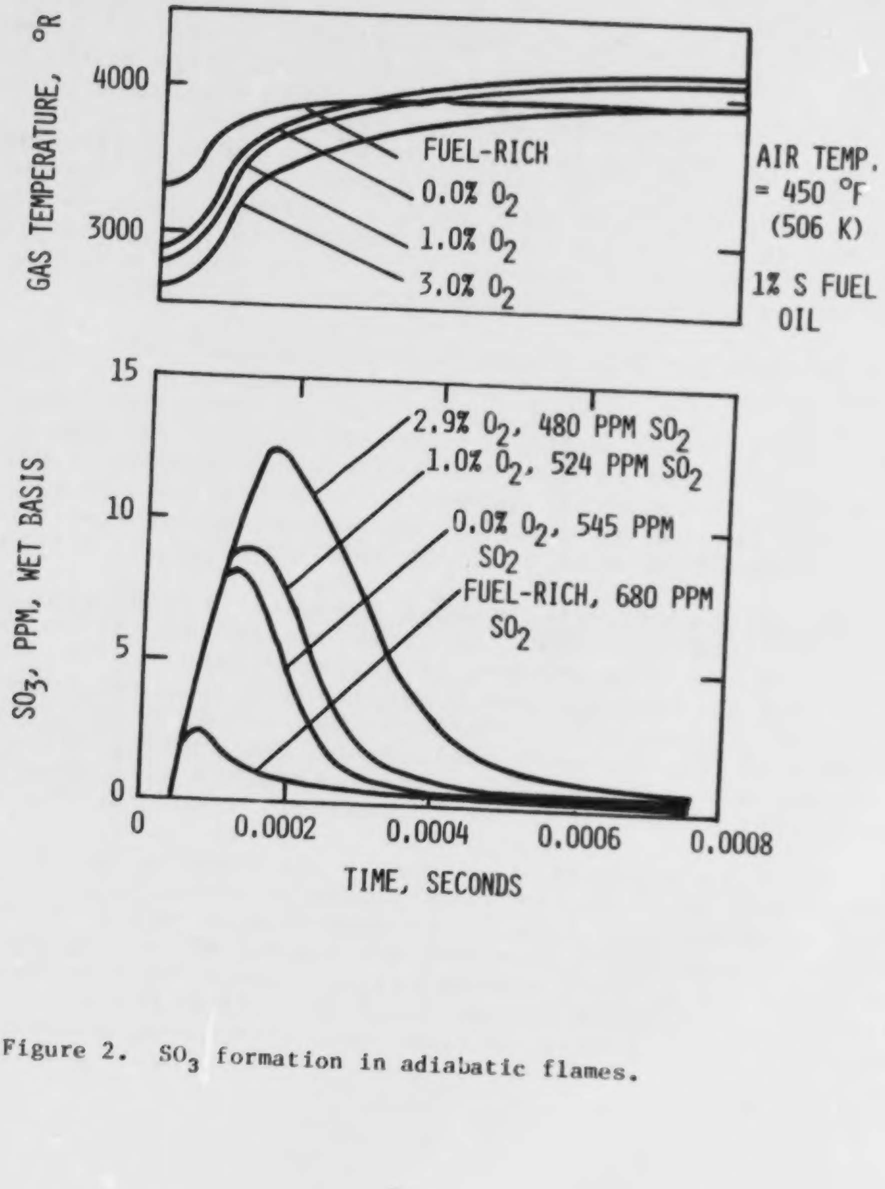

Figure 2. SO_3 formation in adiabatic flames.

to 2.5% conversion at 3% O_2. These peaks are consistent with observed conversion levels in stack gases. However, SO_3 levels decay rapidly back to less than 1 ppm. The time at which SO_3 peaks corresponds to the point at which O atom concentration becomes sharply reduced. This point is reached when CO approaches equilibrium. It is possible that turbulent mixing could result in alteration of the decay process or that distributed mixing in diffusion flames could sustain high O atom concentrations for longer periods of time. Investigation of these possibilities represents an area for further analysis. However, based on the current results, it appears unlikely that flame produced SO_3 is the major source of stack gas SO_3. The computed SO_3 profiles are similar to measured profiles presented by Levy (3)(5)(7), Merryman (6), and Hedley (8). However, the computed profiles decay much more rapidly than the profiles in the referenced works which extend out to as long as 0.2 seconds before returning to equilibrium. This difference is attributed to the significantly lower temperatures in H_2S and COS flames used in the referenced work, but a more detailed examination is warranted.

Conclusions from these calculations are that reduction of O_2 level and the use of fuel-rich combustion can be expected to reduce SO_3 levels in the flame. Use of additives to reduce O atom concentration would also be effective. It appears unlikely that SO_3 produced in the high temperature adiabatic part of flames can escape to the stack gases at concentrations in excess of flame equilibrium levels, but further investigation with more detailed combustion models and/or test programs is warranted.

Formation of SO_3 in Cooled Flames--Thermodynamic equilibrium considerations show that, as gases containing sulfur as SO_2 and SO_3 are cooled, the percent of sulfur present as SO_3 can increase up to 100% at temperatures corresponding to power plant air heater and stack temperatures. Factors that are expected to influence the rate of SO_3 increase include the gas cooling rate and mixing of excess air. Computations were performed with the KVB one-dimensional kinetic program to evaluate these two factors.

There is a two-fold effect in gas cooling as heat is transferred from the flame by radiation and convection. First, at flame temperatures there is an appreciable amount of dissociation so that all CO and H_2 are not all converted to CO_2 and H_2O. As the gases are cooled, recombination occurs as necessary to maintain equilibrium at the local gas temperature. If cooling occurs at a rapid rate, O atom concentrations, although decreasing, will exceed equilibrium, and SO_3 will be produced by

$$SO_2 + O + M \rightleftarrows SO_3 + M$$

As in the adiabatic flame, SO_3 concentrations in excess of that for $O-O_2$ equilibrium can be produced. The second effect involved is the temperature dependency of the O production reaction rates. The three-body SO_2-SO_3 reaction is not temperature dependent but the O atom reactions are. At low temperatures the O atom formation will be slow so that $O \rightarrow O_2$ and SO_3 formation will deplete O atoms, and SO_3 concentrations will stabilize at a constant level.

Air mixing into hot gases can be expected to produce similar results, first causing completion of combustion, then cooling with recombination reactions, and finally quenching the reactions.

Computations with flame cooling have been performed for a range of fuel-air ratios and cooling rates. Cooling was initiated at 0.001 second, the point at which the combustion reactions had essentially reached equilibrium previously as shown for the adiabatic flame. Based on data of James (13) boiler gases cool approximately 1000°F (555 K) in the furnace before entering the superheater. Furnace cooling rates are of the order of 10°F per foot (18 K/m). In the superheater and air heaters higher rates of the order of 100°F per foot (180 K/m) are estimated. Computation was performed with an assumed gas velocity of 100 feet per second (30.5 m/s). Figure 3 presents the profiles of temperature and SO_3 formation as a function of time at 3% O_2. Gas temperature drops 1000°F (555 K) at a rate of 10°F per foot (18 K/m) simulating furnace conditions, then at a rate of 100°F per foot (180 K/m) simulating superheater and heat exchanger conditions. SO_3 level remains below 1 ppm throughout the furnace and rises sharply to 8 ppm (1.6% conversion) at the point of increased cooling rates. This level of conversion is consistent with levels observed in operating plants. For calculations with faster cooling rates SO_3 was higher, indicating a greater O atom imbalance as expected. Formation of SO_3 is quenched when temperatures drop below 1540°F (1111 K) at least for this condition of about 3% excess oxygen. At this point O atoms are depleted.

The influence of oxygen content was also investigated. Figure 4 shows the computed profiles of temperature and SO_3 versus time for four levels of excess O_2 and a cooling rate of 1000°F per foot (1823 K/m). SO_3 rises most rapidly when gas temperature drops from 3000°F to 2000°F (1920 K to 1370 K). The effect of excess oxygen is most pronounced below 1% O_2 with only a slight increase in SO_3 at 3% O_2.

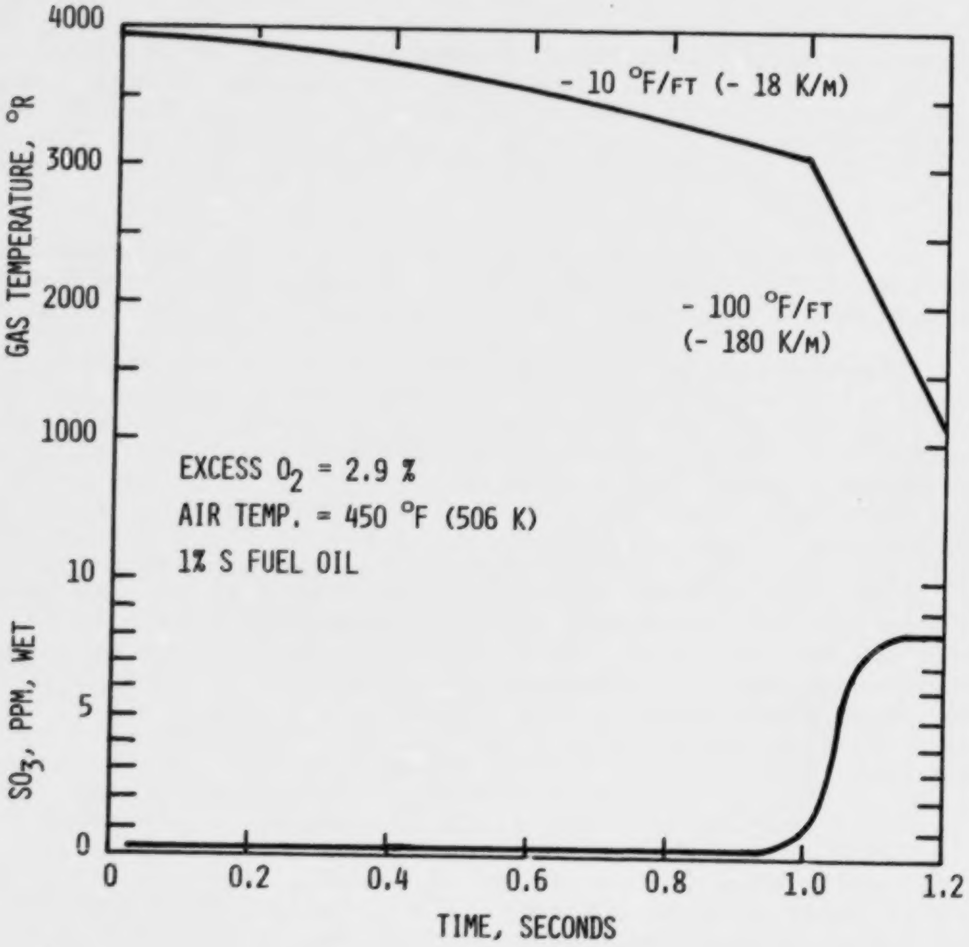

Figure 3. SO_2 formation in a cooled gas.

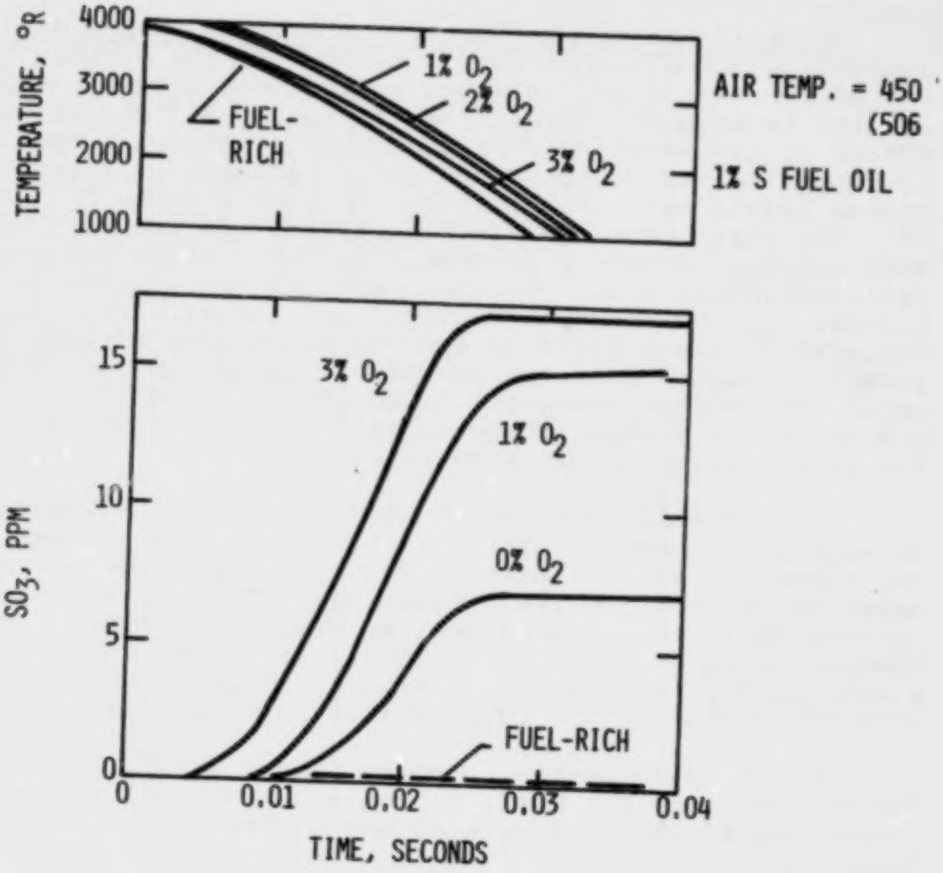

Figure 4. Effect of O_2 on SO_3 formation.

The computed effect of excess O_2 on percent conversion of SO_2 to SO_3 was compared with measured data from various boilers (14-20), shown in Figure 5. The computed conversion is much higher than test data at zero excess O_2. However, the SO_3 increase, as O_2 is raised, is consistent with the data. A tendency for SO_3 conversion to level off above 3% O_2 is apparent in both computed and measured data.

Formation of SO_3 in Cooled Flames With Staged Air--Fuel-rich combustion accomplished with a portion of the furnace burners out of service or air bypassed above the burners are combustion control techniques currently employed for NO_x reduction. The effect of air addition to a fuel-rich mixture has been computed by repeating the computed fuel-rich solution of Figure 4, but mixing additional air sufficient to increase the O_2 level to 3%. The point of air mixing initiation and the rate of injection were varied. Figure 6 presents the temperature and SO_3 concentration profiles versus time. Curves A are for the completely fuel-rich mixture with no mixing. Curves B are for air injection in high temperature gases prior to cooling below 3000°F (1920 K). SO_3 formation begins near the end of air injection and continues until the temperature drops below 2000°R (1540°F, 1111 K). Twenty ppm of SO_3 is formed, compared with 17 ppm for the case where the entire flame is at 3% O_2 (Figure 4).

Curve C shows the effect of decreasing the rate of air mixing by adding the same quantity of air over a longer time. The initial SO_3 formation rate is slower, but the final level is higher compared to Curve B. Curve D shows the effect of delaying the injection until the temperature has dropped to 2000°F (1111 K). CO combustion is slower at this condition but does react and causes a much higher level of SO_3. With air mixing initiated at 1400°F (778 K), Curves E, the CO is unable to react and no SO_3 is formed.

Nitric oxide levels computed in the foregoing cases showed a 66% NO reduction for Curve B compared with that for air-rich combustion at 3% O_2 (Figure 4) and negligible NO formed for Curves A, C, D, and E. This is consistent with the effects found in power plants when fuel-rich combustion is employed so that heat is lost from the flame prior to and during air addition.

It is interesting to note that formation of NO, as for SO_3, occurs as a result of O atom reaction (9). However, the equilibrium levels of NO at flame temperatures are very high and decrease with temperature in contrast to SO_3. The NO formation

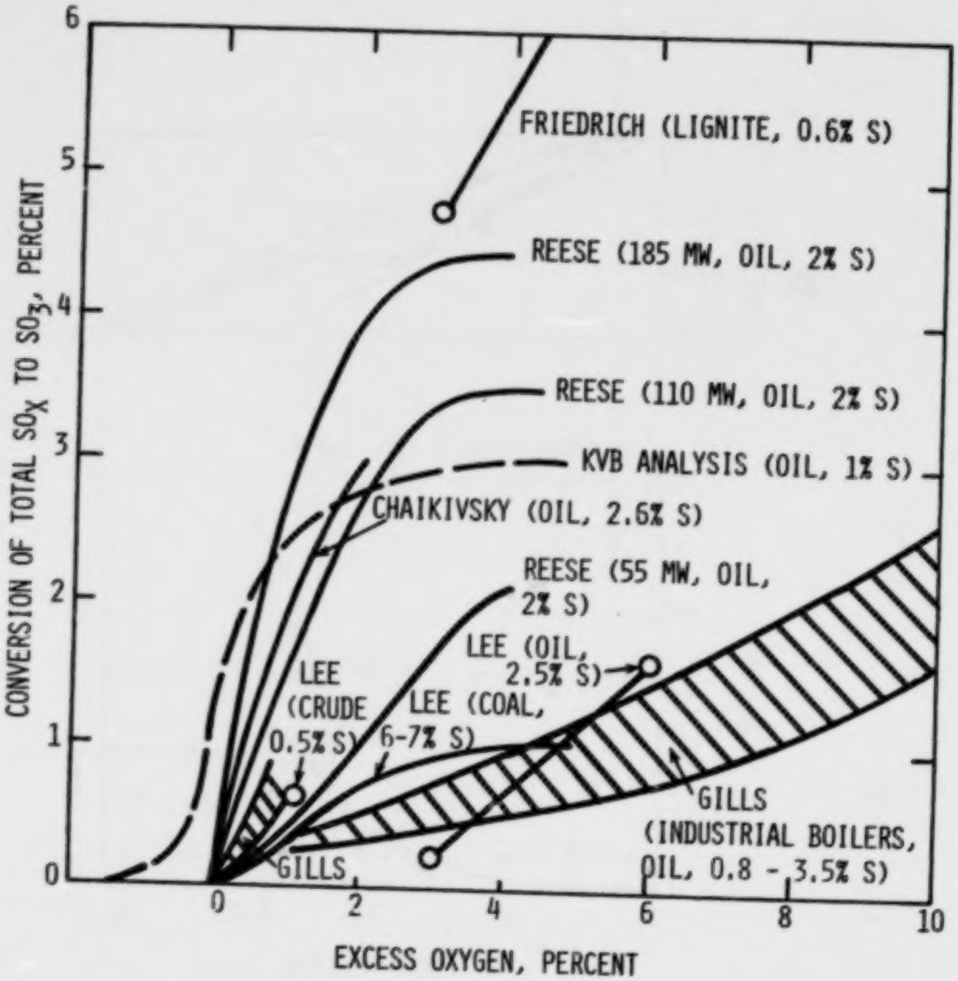

Figure 5. Effect of O_2 on SO_3 emissions.

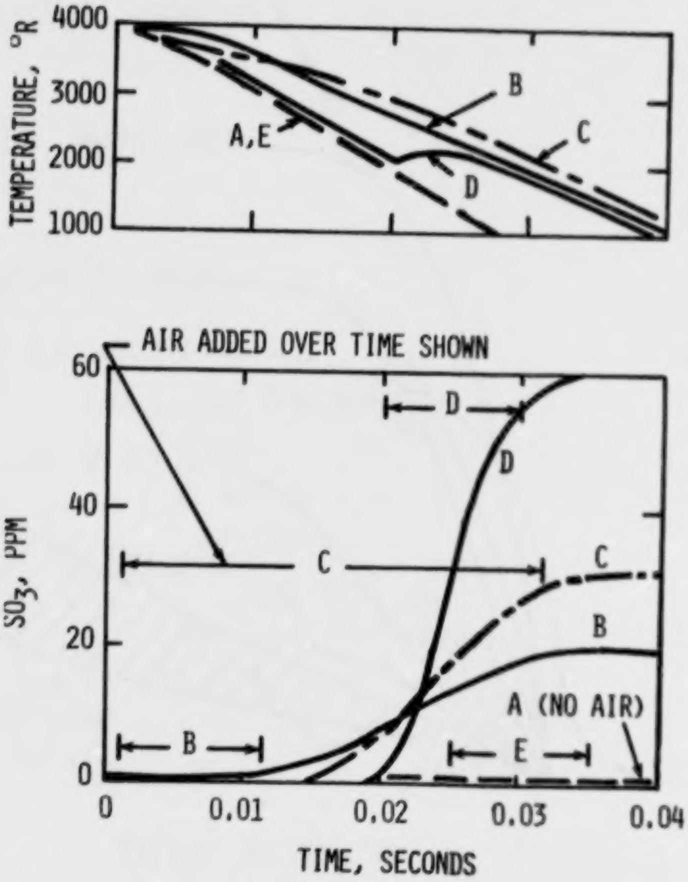

Figure 6. Air addition in a fuel-rich flame.

rates are much slower than for SO_3, and NO levels increase continuously, requiring times of the order of 0.05 seconds to reach levels observed in power plants as discussed by Breen (9). As temperatures drop by cooling and bulk gas mixing, the NO is frozen and remains present at low temperatures. These basic differences between the equilibrium and kinetic characteristics of NO and SO_3 indicate that differing requirements may arise in attempting simultaneous control of these two emittants. Fortunately the basic technique of reducing excess air is beneficial in reduction of both.

From the results of air addition computations and comparison with the work of Barrett (21) and also Hedley (8), it is apparent that, to minimize SO_3, air mixing to high levels of excess oxygen should be avoided in the temperature range of 2000° to 3000°F (1367 to 1920 K). The use of fuel-rich combustion, together with careful staging of air addition, appears to be a possible technique for minimizing both NO and SO_3 formed by gas phase reactions. Further work is necessary to define the mixing criteria necessary to achieve this result. Experimental investigation of the effect of staged combustion on SO_3 has not yet been conducted.

Test measurements of SO_2 and SO_3 frequently indicate that the percent conversion of sulfur to SO_3 increases as fuel sulfur content decreases. However, the SO_3 kinetic reactions are such that SO_3 formation rates are directly proportional to SO_2 concentration. This suggests that for a given flame condition the percent conversion to SO_3 would be constant and independent of fuel sulfur content. The kinetic computations described above were re-performed with fuel oil sulfur contents ranging from 0.5% to 2.5% sulfur. The computed SO_3 levels changed in direct proportion to sulfur content, i.e., percent conversion to SO_3 remained constant. The increase in conversion observed in test data is believed, therefore, to be the result either of test method inaccuracy or possible catalytic surface effects.

TEST METHODS

Methods Evaluated

Over a period of several years, KVB has used three wet chemistry methods (other than EPA Methods 6 and 8) for SO_2 and SO_3 measurement: the Shell-Emeryville method (22), the South Coast Air Quality Management District (SCAQMD) method (23), and the Goksoyr/Ross controlled condensation method (24). SO_2 has also been measured with continuously-recording electronic monitors. This section compares results obtained with these methods.

Shell-Emeryville Method--The Shell-Emeryville method uses the same chemicals as EPA Method 8. Ninety percent isopropanol solutions are used to selectively absorb SO_3 and a H_2O_2 solution follows for the SO_2 absorption. The SO_2-SO_3 fractions are titrated with lead perchlorate to a sulfonzo III end-point. The SO_3 results obtained tend to be somewhat high because of problems associated with the use of the IPA solution--specifically the nitrogen purge to remove interfering SO_2.

SCAQMD Method--In this method, H_2SO_4 mist particles are collected on a Whatman thimble paper filter prior to absorbing the SO_2 in a solution of 5% NaOH. The thimble is maintained at 165°-200°F (350-370 K) to prevent the condensation of water vapor but permit the collection of H_2SO_4 mist particles. There are questions about the efficiency of the paper filter as a means of collecting SO_3. Because there may be incomplete aggregation of H_2SO_4 mist particles, the SCAQMD method may produce SO_3 measurements on the low side.

Goksoyr/Ross Controlled Condensate Method--This method has desirable features of separating the SO_2, $H_2SO_4(SO_3)$, and particulate matter from flue gases in a clean manner. The $H_2SO_4(SO_3)$ is separated from the rest of flue gases, including SO_2, by cooling the gas stream below the dewpoint of H_2SO_4 but maintaining the temperature of the gases above the water dewpoint.

Particulate matter is removed by means of a heated quartz glass filter in a filter holder kept above 500°F (533 K). A condensation coil where the H_2SO_4 is collected is maintained at 140°F (333 K) by a water circulation bath. Sufficient residence time is allowed to condense all the acid present. The SO_2 is then removed in impingers filled with H_2O_2.

Modified Controlled Condensate Method--This procedure is similar to Goksoyr/Ross coil but uses an air-cooled coil to collect the acid. The sampling rate is higher and a larger sample is taken. One drawback in this procedure is that the control of the coil temperature is not as effective.

KVB has accumulated considerable experience and data using these methods in various field tests of combustion and process devices. The results of conversion to SO_3 have been consistent at SO_2 levels above 100 ppm with a lower shelf of measurements at 3 ppm to 4 ppm SO_3 at lower SO_2 levels. In some cases the percent conversion to SO_3 apparently increases at reduced sulfur dioxide levels. However, this may be a result of inherent lower limits in the accuracy of measurement methods rather than what is actually happening as a chemical process.

SO_2, SO_3, AND SULFATE EMISSIONS DATA

Sources Evaluated

The data shown in this section were excerpted from KVB studies of:

1. Industrial process exhausts using the Shell-Emeryville and SCAQMD chemical methods and an SO_2 analyzer (25).
2. Industrial boiler exhaust using the Shell-Emeryville methods (26) and the SASS train (27).
3. Utility boiler exhaust using a modified controlled condensate method (28).
4. Diesel engine exhaust using the Goksoyr/Ross and Shell-Emeryville methods (29).
5. Mid-sized coal-fired utility boiler exhaust using the Shell-Emeryville method (30).
6. Gas turbine exhaust using the Shell-Emeryville method (28).

Industrial Process Sources

In a survey for the California Air Resources Board, 38 industrial process sources were tested. These were all non-combustion sources of SO_x including glass furnaces, sulfuric acid plants, sulfur recovery plants, coke kilns, cement kilns, fluid catalytic crackers, gypsum kettles, incinerators, lead furnaces, iron cupola, iron ore sintering machines, blast furnaces, and steel open hearths. This program included a comparative evaluation of the Shell and SCAQMD methods for SO_x.

Figures 7 and 8 show a comparison of instrumental SO_2 measurements versus wet chemical SO_2 results for two methods. In Figure 7, a consistent trend is apparent which shows that the results for the Shell-Emeryville wet chemical method are approximately 9% lower than the instrumental reading for SO_2. Almost all the points are above a 45° diagonal which denotes the line of coincident agreement.

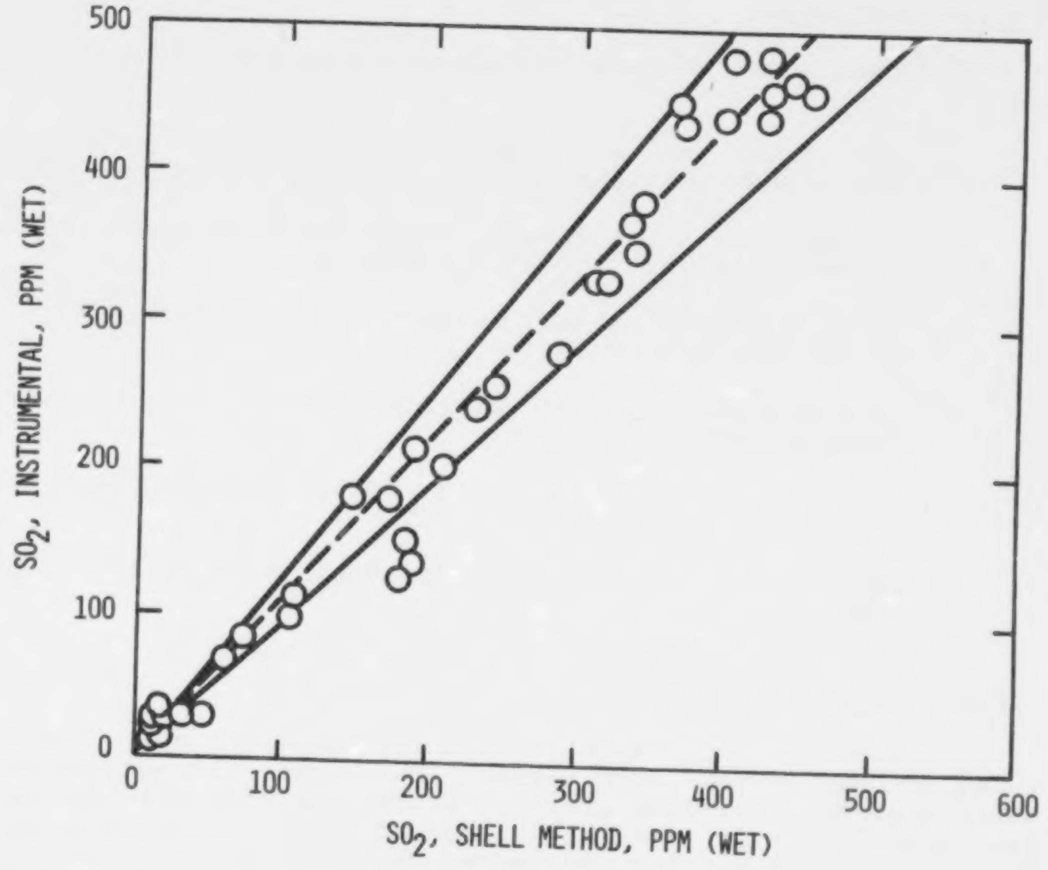

Figure 7. Comparison of SO_2 instrumental and SO_2 Shell method results.

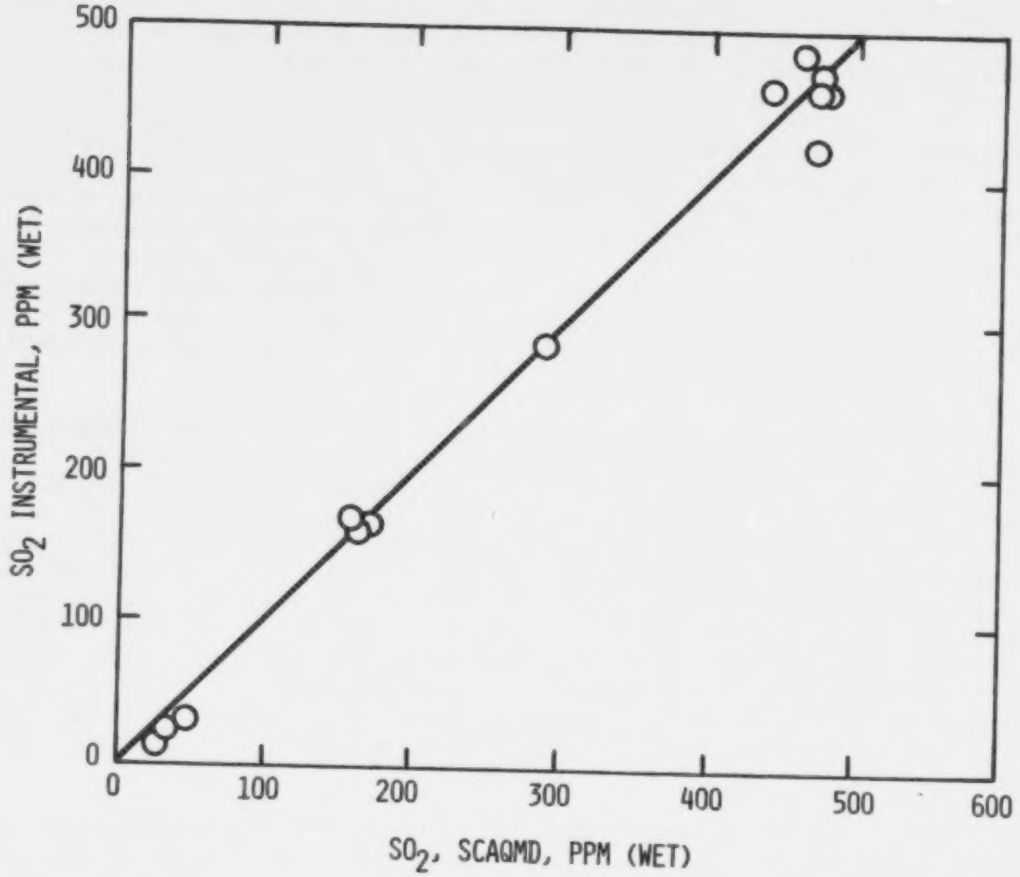

Figure 8. Comparison of SO_2 instrumental and SO_2 SCAQMD method results.

A statistical analysis of the Shell-Emeryville data, excluding the three points at 190 ppm, showed the mean instrumental/wet measurement ratio to be 1.088. There was a 90% probability that ratio would lie between 0.97 and 1.21 for any particular experimental measurement. It has been reported that SO_2 values between 5% and 10% below true values were found using a method with H_2O_2 solution in small impingers. In a similar plot for the SCAQMD method (Figure 8), the agreement between the instrumental and wet chemical method appears more satisfactory.

During these tests, the wet chemical methods were also checked by absorbing measured quantities of certified SO_2 calibration gases used for calibrating the UV analyzer. Results for SO_2 using the Shell-Emeryville were 5% to 6% low in those tests. The field test results for SO_2 as measured by the Shell-Emeryville method were corrected by the ratio of 1.088 to obtain closer agreement with other methods of measurement. When the SCAQMD method was used, the SO_2 results were reported directly. The results reported for the wet chemical analyses were obtained by average of the replicate samples (normally three).

The SO_3 experimental results for the Shell and SCAQMD methods that were obtained on common tests are shown on Figure 9. Points for total sulfate which were obtained with the SCAQMD method are also shown. SO_3 results measured by the SCAQMD method were as high as those measured with the Shell method in only one case. In all other cases they were lower. These results are consistent with previous discussion where it was indicated that SO_3 results obtained with the Shell method might be high, especially at low total SO_x, and that the SO_3 results obtained with the SCAQMD method would be low, if anything. The amount of data obtained is insufficient to determine which method, in fact, records more accurate values of SO_3. Both methods suffer from a lack of adequate calibration procedures.

Experimental results for the SO_3 versus SO_2 employing the Shell method are summarized in Figure 10. For tests where the total SO_x concentration was greater than 50 ppm, there was only one case where the percentage SO_3/SO_x ratio was as much as 10%. For that particular device (a coke calcining kiln), a value of 10% is not unreasonable because of high stack temperature (1800°F, 1260 K). In three other cases the percentage SO_3 was greater than 4%. It was 4% or less for all other cases where the total SO_x was greater than 50 ppm. At total SO_x values less than 50 ppm, however, the percentage SO_3 was greater than 10% in most cases and in some cases greater than 20%. These excessively high values are believed to be related to the limited amount of SO_2 that is dissolved in the isopropyl

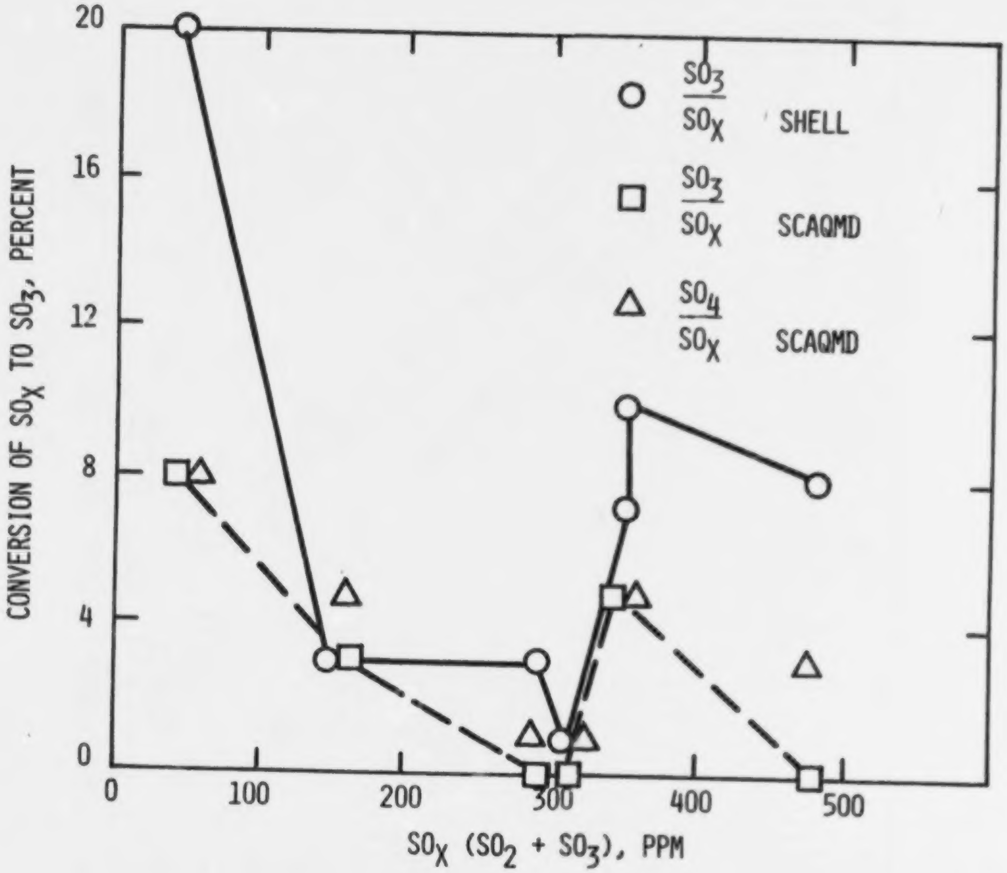

Figure 9. Comparison of Shell and SCAQMD SO_x methods.

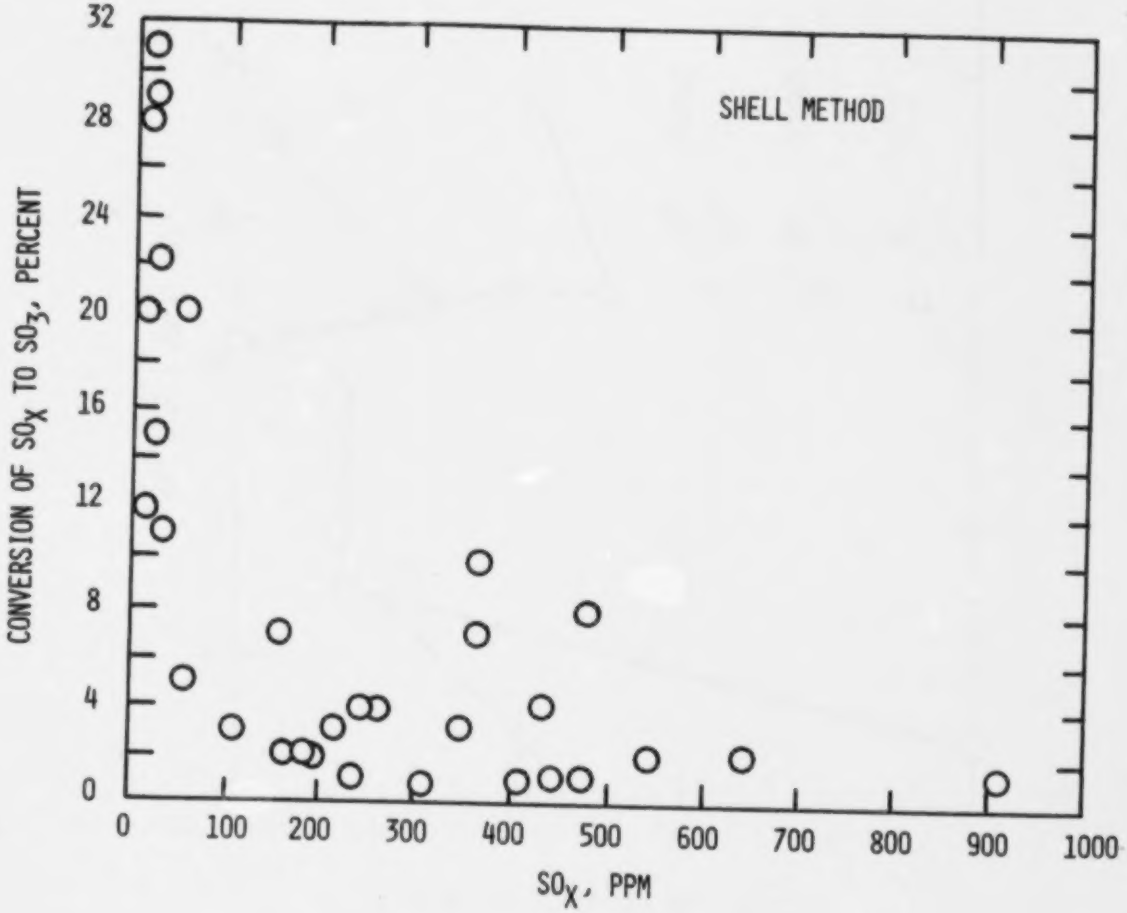

Figure 10. SO_3 emissions from industrial processes.

alcohol solutions and which is not removed by purging. This residual SO_2 remains to be measured as SO_3. Of course, the smaller the total ppm of SO_2 in the sample gas, the more important this residual SO_2 could become.

Although it is not clear at what point the residual SO_2 may become important in determining the reported SO_3 concentrations, it seems that below total SO_x concentrations of 50 ppm-100 ppm the reported SO_3 concentrations should be viewed with some skepticism when obtained by wet chemistry separation.

Industrial Boilers SO_2/SO_3 Data

SO_2/SO_3 data were reported for various industrial boilers under EPA contract 68-02-1074 (26). The method of analysis was the Shell-Emeryville method. Figure 11 shows the percent conversion of total sulfur oxides, SO_x, to SO_3 was typically 1% to 2% except when sulfur oxide concentrations dropped below 500 ppm. The steep rise below 500 ppm was attributed to the measurement method itself. There appeared to be no strong effect of fuel type other than its sulfur content. For example, No. 6 oil data decreased with total sulfur oxides just as with other fuels. For coal, the type of coal feed did not have a significant effect on the SO_3/SO_x conversion in the exhaust gases. The coal feed types included spreader stokers, pulverizers, underfeed stokers, and cyclones.

The SO_2 emissions for these industrial boilers were related to fuel sulfur content as shown on Figure 12. The SO_2 emissions with fuel oil were generally with ± 100 ppm of that based on 100% conversion of S to SO_2. However, deviations of up to 300 ppm were noted. With coal there is much more scatter. For fuel sulfur over 3%, SO_2 emissions were only 50% to 75% of 100% conversion. This is attributed to retention of the sulfur in the ash.

Retention of S in the ash of coal-fired industrial boilers was investigated to compare the SO_2 emissions with western and eastern coals (30). The results indicated that about 90% of the S was emitted as SO_2 when firing eastern coals, but only about 80% was emitted with western coals. Figure 13 shows the amount of S retained in the ash as a function of total fuel sulfur content. Although there is scatter in the data, there is an indication that the amount of sulfur that is retained tends to be independent of sulfur content.

Industrial Boiler Sulfate Emissions With The SASS Train

Trace species and organics measurements were made on an indus-

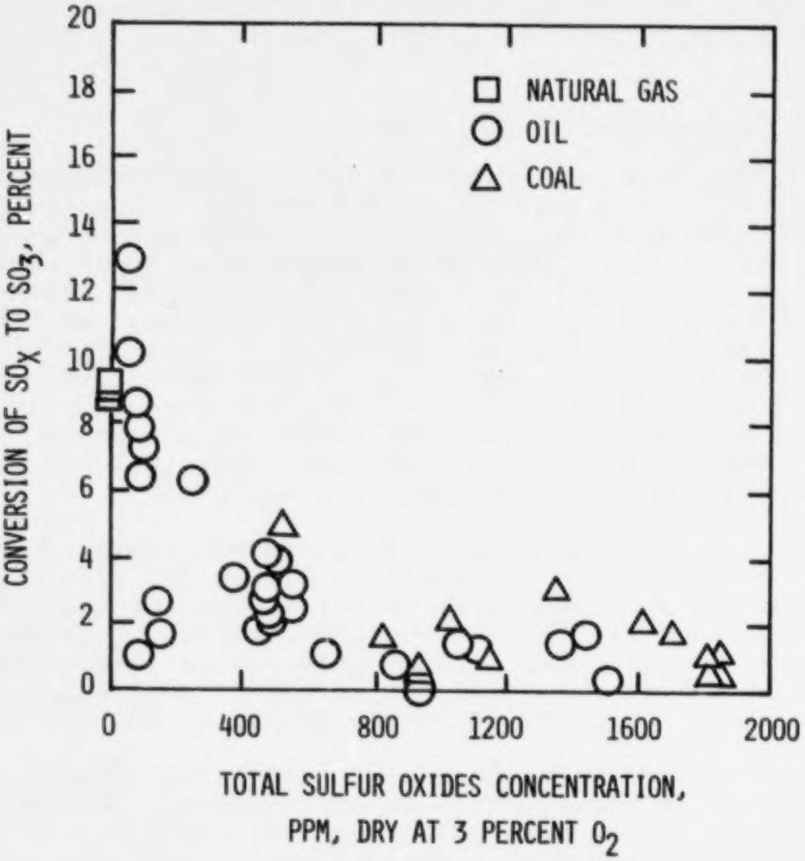

Figure 11. SO_3 emissions from industrial boilers.

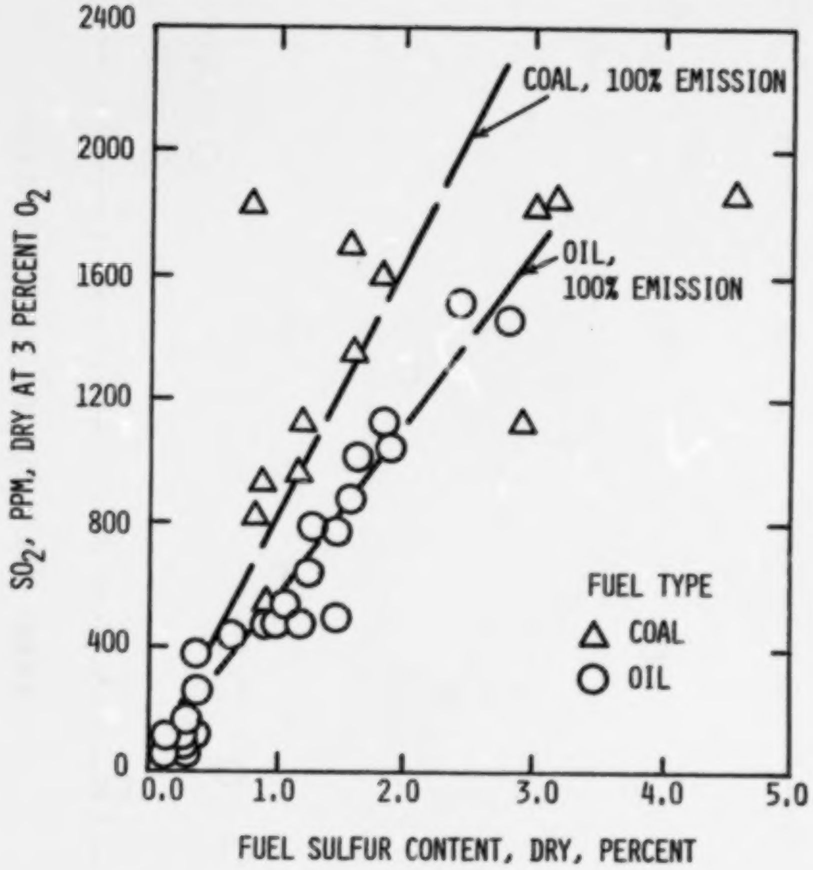

Figure 12. SO_x emissions from industrial boilers.

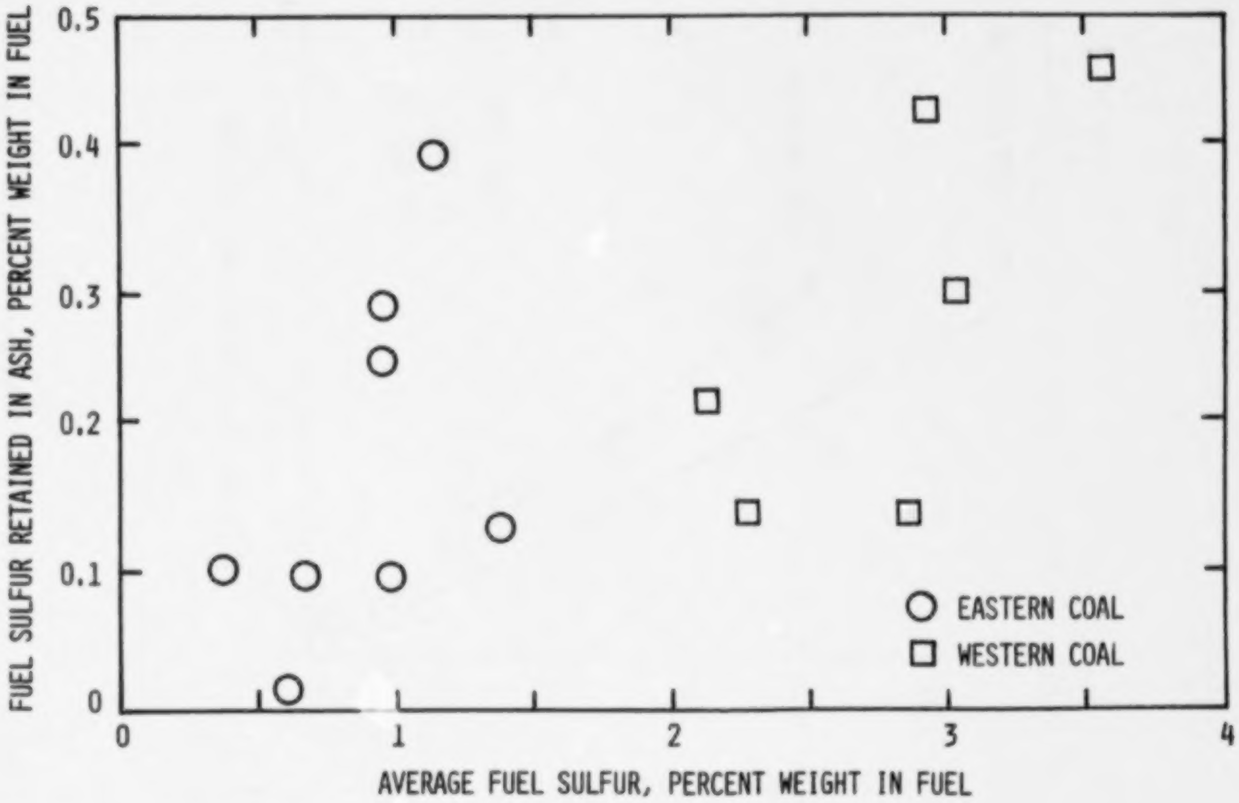

Figure 13. Fuel sulfur retained in ash vs. average fuel sulfur for coal-fired industrial boilers.

trial boiler (27). The EPA Source Assessment Sampling System (SASS) was used and analytical results included sulfates. The data, Table 2, indicate the results for three tests: a baseline test and two tests with combustion modifications. The modifications were flue gas recirculation (34%-35%) and reduced excess air. The fuel was No. 6 oil with sulfur content of 1.0% to 1.2% by weight. The data indicate that most of the sulfur was recovered in the condensate and impingers, mostly SO_2 that passed through the filter. SO_2 emissions were about 2200 mg as SO_2/m^3, which would be 4400 mg/m^3 expressed as SO_4. Total sulfur collected by the SASS was about one-fourth to one-half of the SO_2 emission rate. SO_3 emissions were not measured during these tests, but other tests under similar operating conditions indicated an SO_x to SO_3 conversion of about 1.2% or about 53 mg as SO_4/m^3. Sulfates collected in the cyclones, filter, and XAD-2 organic module were from 18 to 20 mg as SO_4/m^3. About half of the sulfate was collected on the SASS filter, but a large portion was also collected in the XAD-2 module. Based on this very limited test, there was no indication that the use of combustion modifications caused any significant change in total sulfate emissions or in the distribution of sulfates by particle size.

SO_2/SO_3 Determinations Using a Modified Controlled Condensated Method in Utility Boilers

The variation of percentage conversion of total sulfur oxides to SO_3 with total sulfur oxides is shown in Figure 14. The fuels used varied in fuel sulfur content from 0.19% to 0.45%. The results did show a variation with particular units. The percentage conversion to SO_3 averaged 3.4% but was spread over a range of 1% to 6.5%.

Diesel Exhaust SO_2/SO_3 Data

Measurements of SO_2/SO_3 were made by Goksoyr/Ross and Shell-Emeryville wet chemical methods as well as by Dupont UV photometric instrumentation for SO_2 readings.

The results of the Goksoyr/Ross and instrumental SO_2 measurements were found to correlate well for fuel with medium sulfur levels. SO_2 measurements made using the Shell-Emeryville method were lower than by either of the other methods employed.

Figure 15 shows the variation of SO_3 level with sulfur dioxide levels. For nine test conditions, an increase of SO_3 level was observed with increased SO_2 level. The percentage conversion to SO_3, however, varied inversely with sulfur dioxide level.

Table 2. Sulfate Emissions from an Industrial Boiler with Combustion Modifications

Test No.	19-2	19-3	19-4
Condition	Baseline	Low NO$_x$*	Low NO$_x$*
Fuel Sulfur Content, %	1.17	1.18	1.02
Excess O_2	3.00	1.8	1.5
SO_2 Emissions, mg SO_2/m^3	2210	2310	2150
Est. SO_3 Emissions mg as SO_4/m^3	53	55	52
SASS Train Sulfates, mg SO_4/m^3			
10 µm Cyc	1.2	1.1	0.6
3 µm Cyc	NES+	0.74	0.63
1 µm Cyc	NES	NES	NES
Filter	9.5	8.4	9.5
Wash	0.6	1.1	0.53
XAD-2 Resin	0.5	2.1	3.4
XAD-2 Rinse	6	4.5	5.6
Total, Front Half	17.8	17.9	20.3
Condensate, Impingers	2600	1200	2000

*34%-35% flue gas recirculation and lowered excess O_2

+NES = Not enough sample for analysis

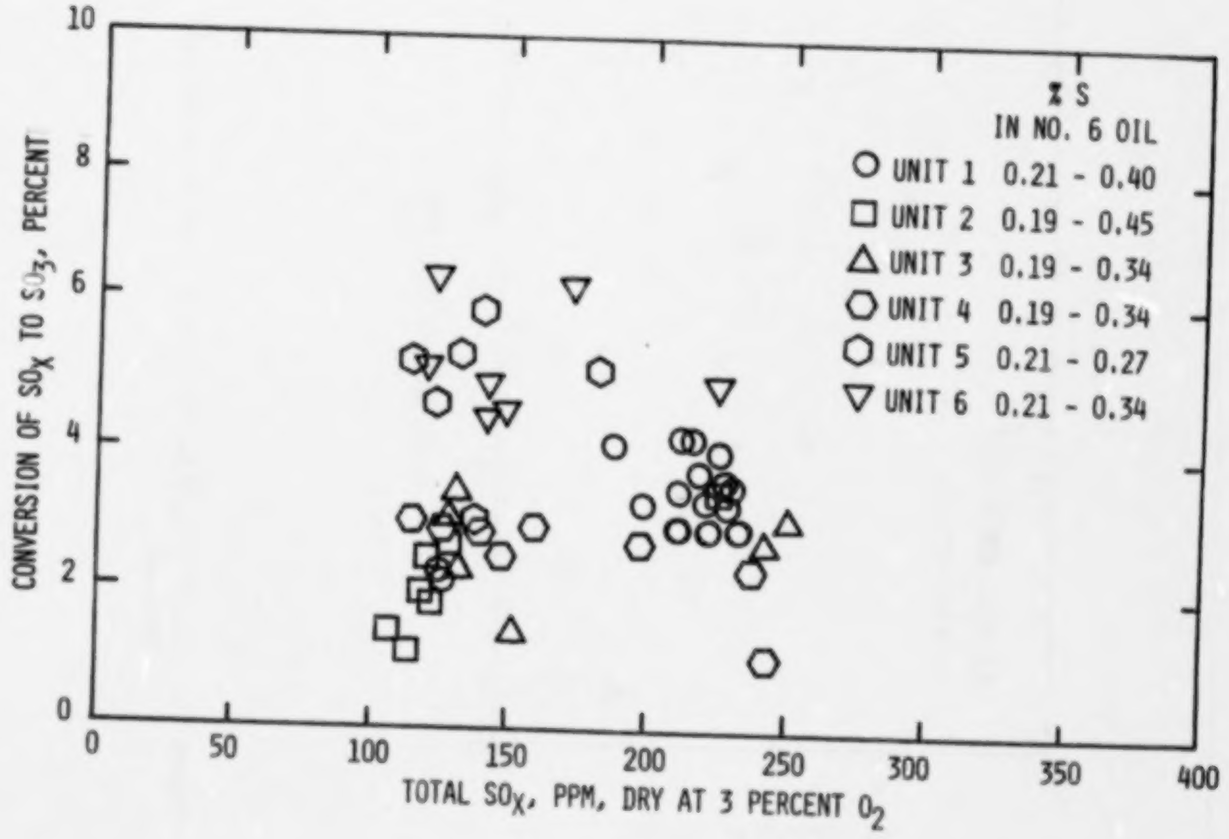

Figure 14. Conversion of SO_x to SO_3 vs. total SO_x in utility boilers.

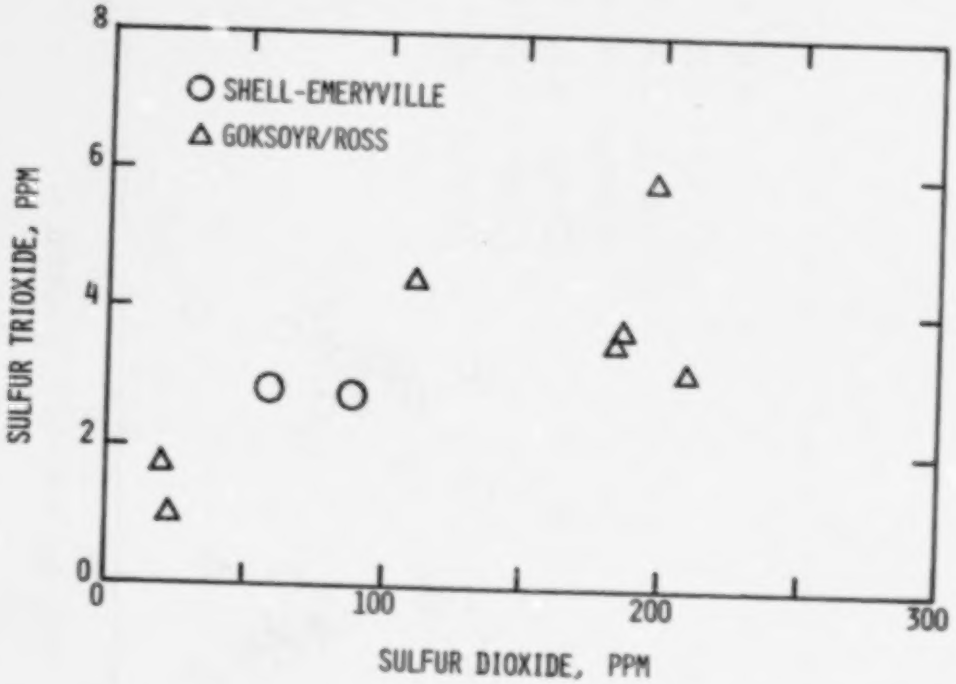

Figure 15. Sulfur trioxide vs. sulfur dioxide in diesel exhausts.

With the Goksoyr/Ross method, and fuel with lower sulfur content, there was an appreciable decrease in SO_3 level. Although insufficient data have been taken to make a definitive conclusion, there does not seem to be a "shelf" value where the method determines the lower level of sensitivity.

In the diesel studies, acid dewpoint temperature studies were also conducted. For a fuel with medium sulfur content, the SO_3 measurements taken employing the Goksoyr/Ross method were used in conjunction with a measured moisture to calculate dewpoint temperature. These calculated dewpoint temperatures correlated closely with dewpoint temperatures measured with a Land dewpoint meter. These results increased confidence in the Goksoyr/Ross method.

Gas Turbine SO_2/SO_3 Emissions

The exhaust gas temperature from a gas turbine is in the range of 1000°F (810 K), and there are no low temperature heat exchangers in the exhaust to provide catalytic surfaces for SO_3 formation. If SO_3 were formed primarily by catalytic action, one would expect to see much lower SO_3 levels from gas turbines as compared with boilers. This is not the case, however; gas turbines produce SO_3/SO_x ratios that are quite similar to those from boilers and other combustion equipment. KVB has measured SO_2/SO_3 emissions from a large number of gas turbines. The majority of that data was obtained for commercial clients and was not, therefore, available for inclusion in this publication. However, the data generally fall in the range of 2% to 6% SO_3 with scatter much the same as shown in previous figures for other devices.

An analytical study of the chemical kinetics of SO_3 formation in gas turbines indicated that SO_2 is converted to SO_3 within the gas turbine combustion chamber in the mid-region of the chamber where hot combustion gases start to be cooled by the injection of excess air. The analysis indicates that SO_3 emissions tend to increase with combustor size and test results tend to confirm that. The analysis also indicated that SO_3 might be reduced by modification of the rate of injection and mixing of excess air. Gas turbines require very close control of excess air mixing to provide a specific shape of temperature profile in the gases entering the turbine wheel. This restraint severely limits the amount of adjustment that can be made in the mixing rates and may preclude any changes to control SO_3. No experimental work in that direction has been conducted.

CONCLUSIONS

Figure 16 shows a plot of SO_3, directly in ppm versus SO_2, from the various measurement methods and sources. There is an apparent lower limit of about 3 ppm to 4 ppm SO_3 that is independent of SO_2. This limit is not readily apparent when percent SO_3/SO_2 is plotted. This value can be attributed to the lower limit sensitivity of the methods, rather than to a real tendency for increased conversion at low SO_2 levels. There was, however, a large degree of scatter that introduced uncertainty.

The Shell-Emeryville method was seen in some determinations to give high SO_3 levels, especially at low fuel sulfur levels. This can be attributed to the method where both SO_2 and SO_3 can be absorbed in the IPA solution. If the inert gas purge is not totally effective, the remaining SO_2 will be trapped and determined as part of the SO_3 fraction.

In the SCAQMD, there may be incomplete aggregation of H_2SO_4 mist particles. This would lead to low SO_3 measurements. The laboratory analytical procedures require significantly greater effort than the simple titration of the Shell or controlled condensate methods.

Using the Goksoyr/Ross and other controlled condensate methods, there are advantages of conditioning the flue gases to separate particulate matter, the SO_3 fraction, and the SO_2 fraction. SO_2/SO_3 separation is accomplished by a physical process. The temperature of the flue gases is reduced below the dewpoint temperature of H_2SO_4 causing a condensation. These results indicate that the controlled condensate methods should produce more reliable and reproducible data less subject to operator influence experienced with the wet chemical separation methods.

The percentage of SO_x emitted as SO_3 appears to be largely independent of the nature of the emission source, i.e., all devices produce about the same level of conversion and show the same degree of scatter in the data. This scatter makes it very difficult to assess any effects on SO_3 emissions that may be caused by operational modifications or other changes. However, the controlled condensate methods appear to offer improved accuracy that may allow such assessments to be made.

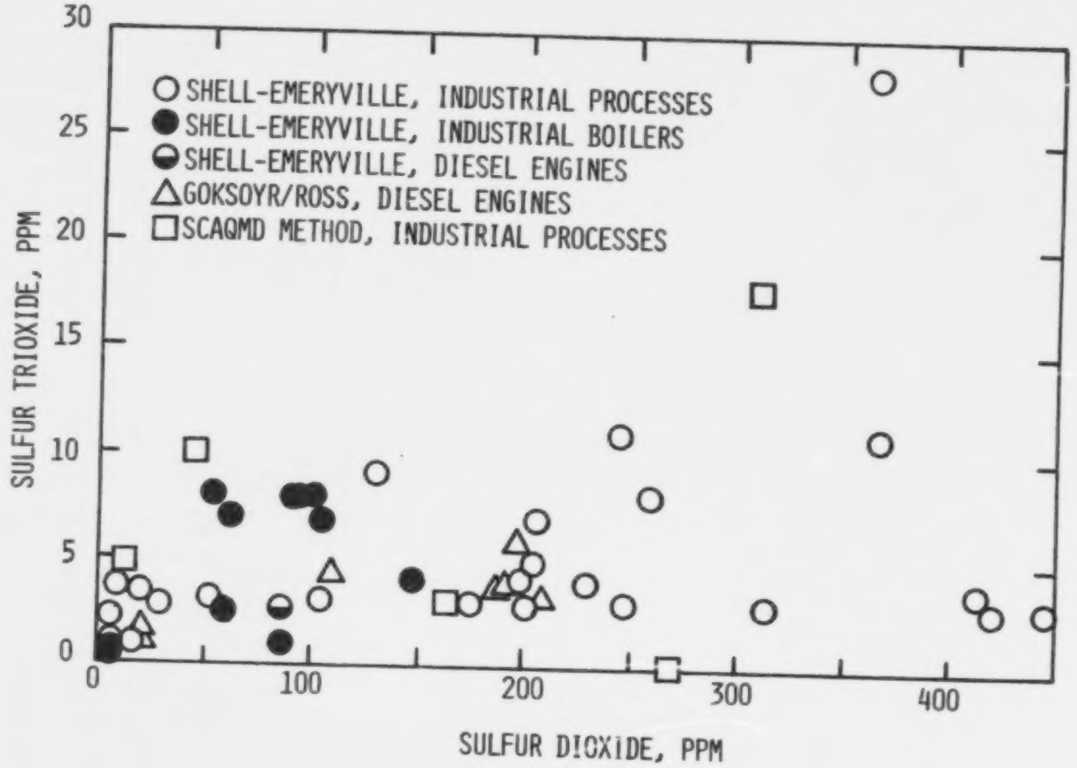

Figure 16. SO_3 vs. SO_2 for three measurement methods.

Analysis of the gas phase kinetics of SO_3 formation indicates that SO_3 can be formed, at amounts typically observed, in the absence of any surface catalysis. The critical temperature range occurs as gases are cooled from 2540° to 1540°F (1670 to 1110 K). Control of the rate of cooling and excess air mixing appears to offer some degree of control over SO_3 formation that warrants further study and as an alternative to the use of additives.

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Some Recent Data on SO_3 and SO_4 Levels in Utility Boilers

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Richard C. Booth
KVB, Inc.

ABSTRACT

A series of recent measurements shed new light on the typical formation processes of SO_3 and SO_4 in utility furnaces fired on high-sulfur oil. Measurements of SO_3 were made using the controlled condensation (Goksoyr-Ross) method, and the filter on the sampling end of the probe was analyzed quantitatively for SO_4 and other constituents. Measurements were made in the superheater at several downstream locations in the convective section and at the air heater outlet of two boilers.

The data suggest that most or all of the SO_3 is formed in the hot section of the furnace and that some of it is converted to SO_4 as the flue gases move through the convective sections of the furnace. Limited data will also be presented on the influence of furnace excess air levels and on the influence of magnesium oxide additives in the fuel.

INTRODUCTION

Furnaces fired on residual oil emit nearly all the sulfur in the fuel in the form of three oxides, SO_2, SO_3, and SO_4. The amounts of the last two are small and variable compared to SO_2, and, to a large degree, a quantitative understanding of the formation mechanism of SO_3 and SO_4 is missing. This must be attributed in part to the difficulty of rapidly and reliably measuring the amounts of either of these substances in the flue gas. The work described here sheds

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some light and raises questions on both the dominant formation mechanisms and the measurement techniques for SO_3 and SO_4.

The work described here is a portion of a program conducted by the Niagara Mohawk Power Corporation at one of their power plants.* The objective of this phase of the work is to minimize emissions of SO_3 gas or condensed acid to help control emissions resulting from corrosion. SO_3 formation can be formed in the furnace area of the boiler by gas phase reactions, or it may be formed in cooler areas of the boiler by the plentiful catalytic oxidation of SO_2. The relative contribution of these potential sources influences the methods chosen to try to reduce stack SO_3 levels as well as the choice of how to assess the effectiveness of an SO_3 reduction program.

Most utility boilers firing high-sulfur oil use additives of some sort to control fouling and corrosion of the superheat areas or to reduce corrosion of the air heaters. The first problem relates to fuel ash constituents such as vanadium and the second to sulfuric acid derived from flue gas SO_3. Catalytic SO_3 formation mechanisms are sensitive to the surface composition of the tubes in the convective passes, which tends to be dominated by the thin layer of accumulated ash and corrosion products. Thus, any change in an additive which feeds this layer may not be reflected in downstream SO_3 concentration for several weeks. However, any effect which a fuel additive has on gas phase formed SO_3 should be apparent as soon as the additive is started or stopped. The motivation for the measurements reported here was first to delineate the relative contribution of gas phase and catalytic SO_3 in the subject boilers, and second to determine the effect of fuel additives on gas phase formed SO_3. Both questions have been partially answered, and some aspects of this work are continuing at the present time.

EQUIPMENT

SO_3/SO_4 Sampling

Gaseous SO_3 was measured using the controlled condensation method (Goksoyr-Ross coil). Flue gas was drawn from the furnace utilizing an air-cooled Pyrex probe. A quartz wool filter at the probe inlet was saved after each test and quantitatively analyzed by wet chemistry for sulfates and magnesium. Pumping and control of the sampling system utilized components from a Method 5 (EPA) sampling train.

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*Niagara Mohawk's sponsoring role and permission to present this work are gratefully acknowledged.

Flue gas extraction utilized a probe, shown schematically in Figure 1, which was intended to hold the sampling tube at relatively constant temperature of 300°F to 450°F while sampling flue gases at temperatures from 250°F to 1400°F. This probe used a Pyrex glass sampling tube inside a double steel jacket. Cooling air flowed toward the probe inlet in the outer annulus and back along the inner annulus, and the air flow rate was manually adjusted to achieve temperatures of about 500°F or below when sampling high temperature regions of the boiler. When sampling colder regions, below about 350°F, the flow was set at a low level and the electric resistance heater was used. Both this heater and the one around the Goksoyr-Ross coil were thermostatically controlled from thermocouple sensors.

A plug of quartz wool was packed into a bowl at the end of the pyrex probe to serve as a filter. This filter operated at temperatures near the flue gas temperature. Each filter was saved and subsequently analyzed microchemically for sulfates and magnesium. The sulfate analysis utilized a water wash of the filter for soluble sulfates, followed by alkaline reaction with peroxide to oxidize any SO_3. Sulfates were then precipitated using BaCl and weighed. The method missed insoluble sulfates and probably reported absorbed SO_2 as SO_4. Magnesium was determined using atomic absorption. O_2 concentrations at the exit of the dry gas meter were measured with a teledyne portable analyzer.

The condensation coil was a blown glass assembly approximately 12 inches long with both the glass coil and a fritted disk surrounded by a water jacket. The glass assembly was wrapped with a small electric heating blanket and fitted into a short length of 3 inch PVC pipe to provide field durability. Operation between 150°F and 200°F was considered acceptable. Subsequent to each test, the condensing surfaces, including the fritted disk, were rinsed repeatedly with 5% isopropyl alcohol. The Pyrex probe was also rinsed, and the total rinse was titrated with NaOH. Early experience showed that roughly one third of the total acid catch could accumulate in the probe.

Sampling utilized the system shown schematically in Figure 2. The probe and coil were followed by one or two impingers to dry the sample, then a small pump and a dry gas meter. Most samples were 1.5 ft^3 collected over about 20 minutes. Frequently titrations were done immediately. Utilizing a crew of two people, it was possible to complete seven or eight tests a day, including the moving of equipment from one part of the boiler to another.

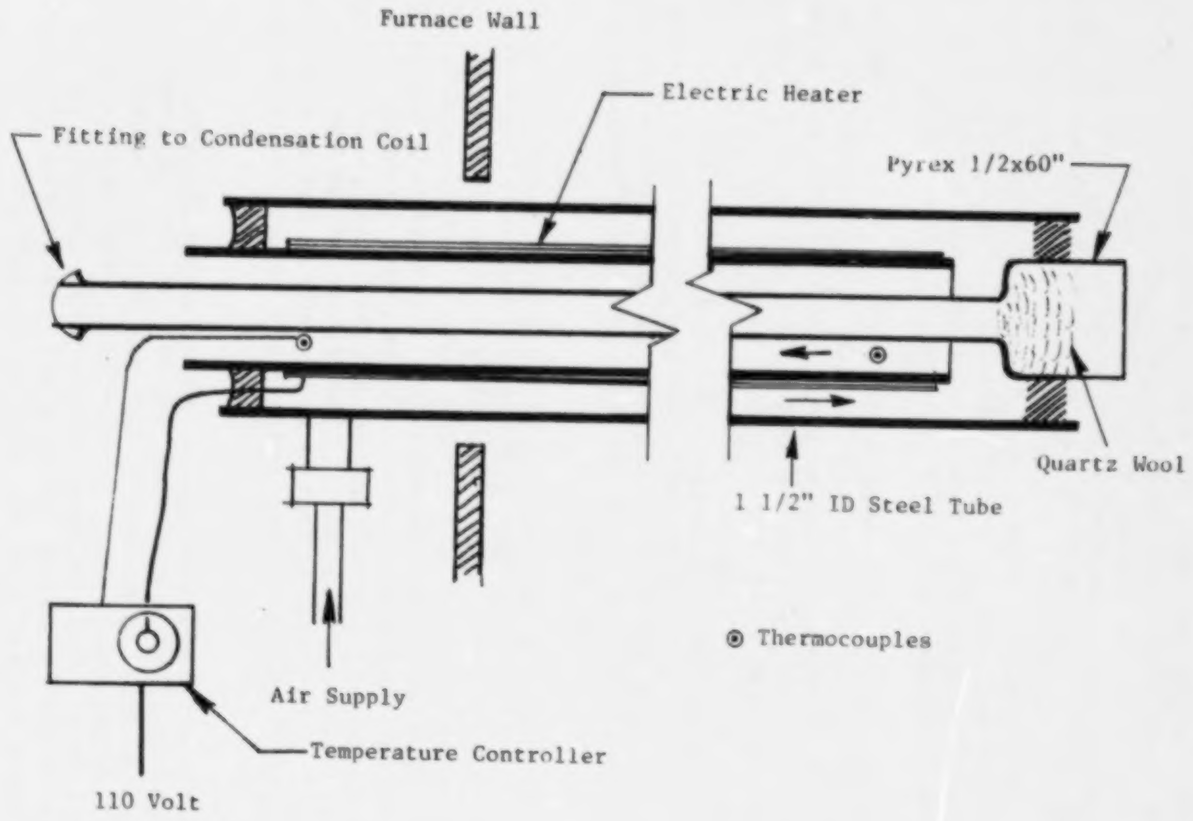
Furnace Wall
Electric Heater
Fitting to Condensation Coil
Pyrex 1/2x60"
Quartz Wool
1 1/2" ID Steel Tube
⊙ Thermocouples
Air Supply
Temperature Controller
110 Volt

Figure 1. Probe for constant temperature sampling.

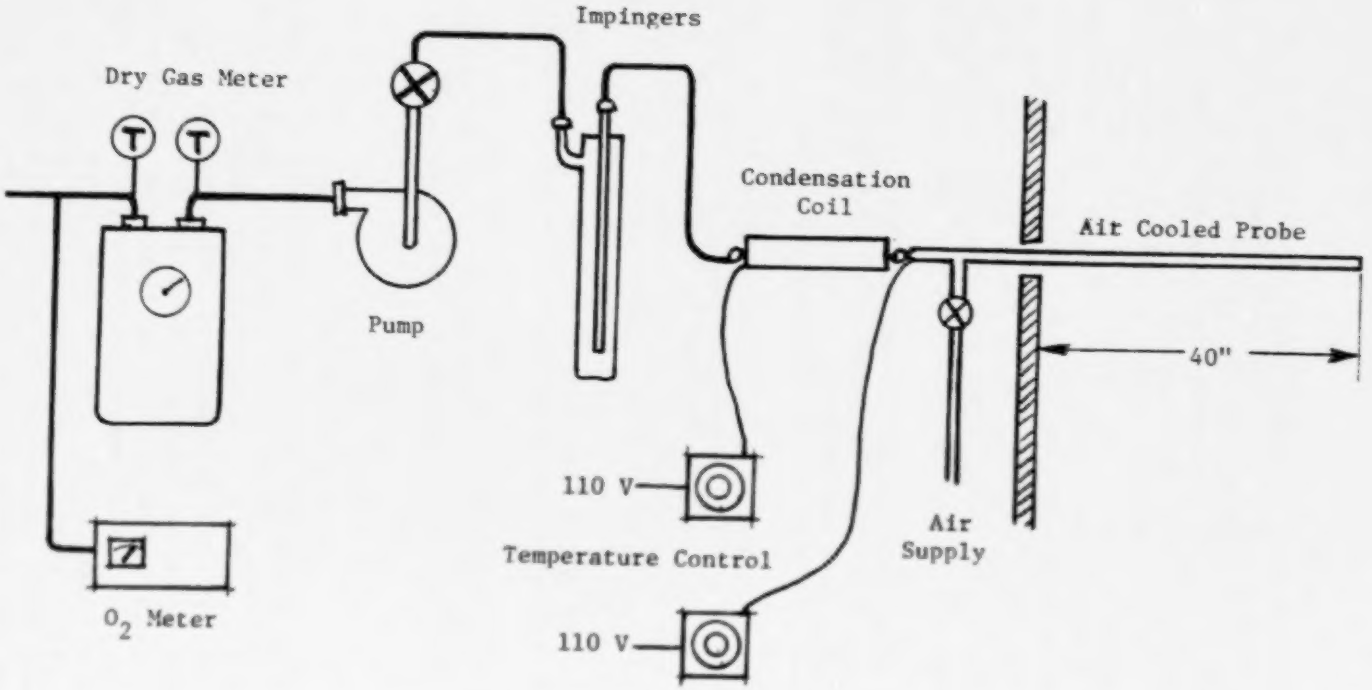
Impingers
Dry Gas Meter
Condensation Coil
Air Cooled Probe
Pump
40"
110 V
Temperature Control
Air Supply
O_2 Meter
110 V

Figure 2. Sampling configuration.

Boilers

Five boilers are in operation at the site, and data on three of them are presented here. Units 2 and 3 are fuel converted (coal to oil) units with nominal 80 megawatt ratings at present. The design of these units promotes substantial stratification in flue gas O_2 concentrations. This probably influences the production of SO_3 and SO_4 and is known to make repeatable measurements of furnace excess air levels either difficult or meaningless. However, deliberate changes in furnace air flows could be meaningfully measured and the effects assessed as long as boiler operation was steady. Both units are equipped with a substantial number of viewing sample ports so that access to the flue gases was not difficult at various points between the superheater and the air heater exit. Figure 3 shows the cross section and various access port locations of Boiler 2.

Unit 5 is a new boiler rated at 850 megawatts. Access to the flue gas on this boiler was available between the economizer and the air heater, between the air heater and the electrostatic precipitator, and downstream of the precipitator.

During this testing all boilers were fired continuously with residual fuel of 2.3% sulfur content. All the boilers use a magnesium oxide based fuel additive to help control vanadium related deposits in the superheat sections. The volumeteric pumping rate for this additive varies from 1/2000 to 1/3000 depending on the boiler. The accuracy or consistency of MgO feed to the boilers is not known. Fuel analysis from a single date on two boilers shows 260 ppm vanadium, 60 ppm magnesium, and 30 ppm sodium.

During all testing, the test boiler was maintained at steady load. Operating parameters relevant to flue gas flow, temperature, and composition were monitored by the test engineer.

RESULTS

Data were gathered over approximately a three-month period on the three boilers. Table 1 is a partial tabulation of data for Boilers 2 and 3. This is a sufficient sampling to indicate the ranges of the various parameters. Present in much of the data is a significant scatter that can be attributed to day-to-day variations in furnace operation (actual excess air levels, choice of burners, etc.) which in many respects cannot be monitored or controlled. The reported O_2 levels are those of the sampled gases and are not representative of furnace excess air levels. All concentrations have been corrected to a standard air dilution of 3% O_2. The sampling and laboratory procedures were of high quality, and instances of obvious error have been deleted.

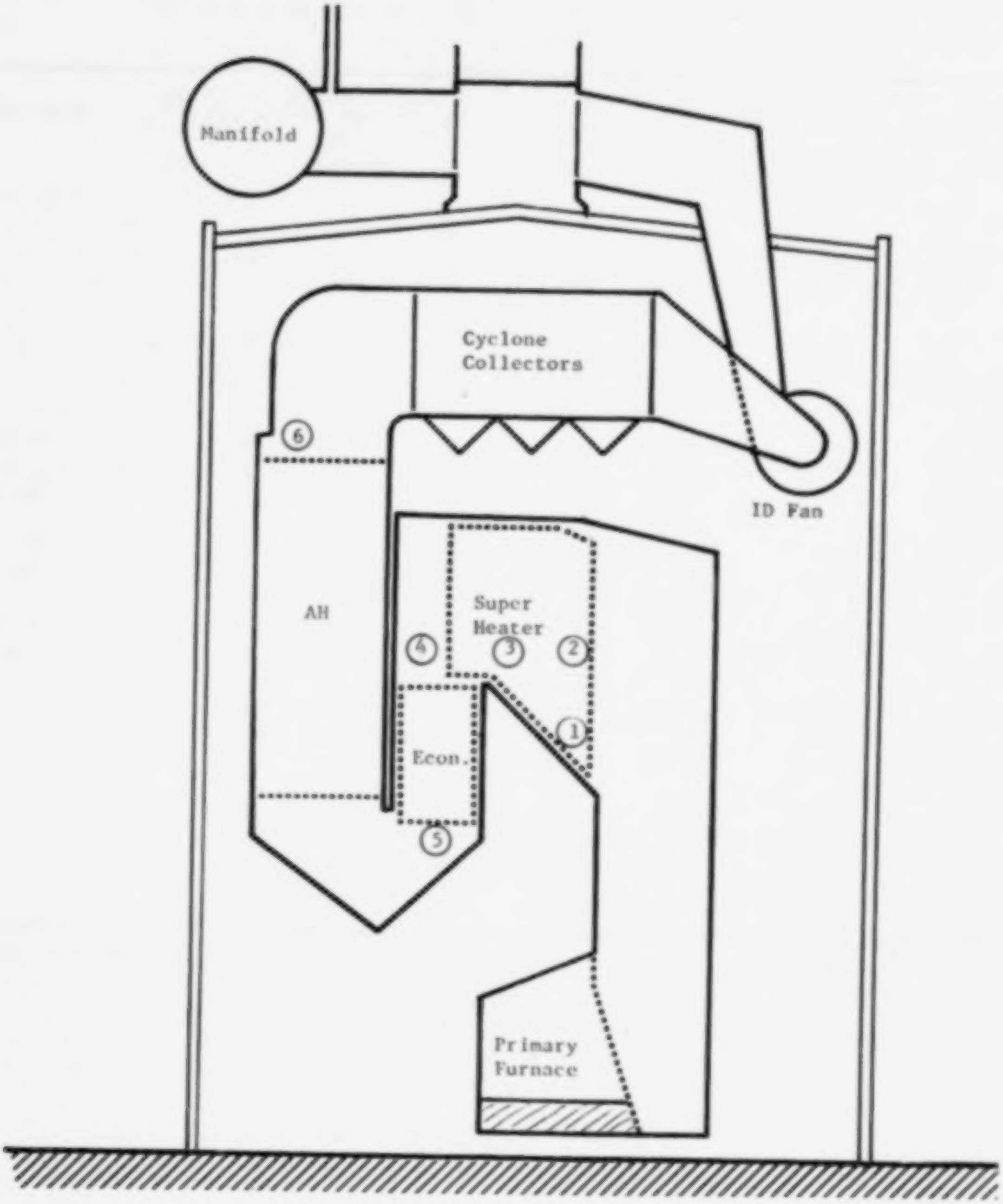
Manifold
Cyclone
Collectors
⑥
ID Fan
AH
Super
Heater
④
③
②
①
Econ.
⑤
Primary
Furnace

Figure 3. Cross section of furnace with sampling locations.

Table 1. Partial Listing of SO_3/SO_4 Data

Test	Location[a]	O_2[b] (%)	Temp. (°F)	ppm by Vol @ 3% O_2				Operation
				SO_3	SO_4	Total	Mg	
1A	2-1	7	1170	16	13	29	16	Normal
1C	2-2	3	1380	19	8	27	11	"
1E	2-3	3.9	1065	13	14	27	10	"
1G	2-4	2.5	865	16	10	26	4	"
2A	2-6	9.4	315	15	21	26	3	"
2B	2-6	7.5	440	27	6	33	1	"
2E	2-6	8.9	380	21	16	37	3	"
3A	2-5	8.6	645	11	24	35	13	Normal
3C	2-1	7.5	1190	25	10	35	4	No Additive
3F	2-1	7.0	1190	12	15	27	11	Normal
4B	2-1	4.6	1250	25	9	34	17	Normal
4C	2-1	2.0	1180	9	11	20	12	Low Air
5A	2-5	2.8		12.6	13	26	7	Normal
5C	2-5	1.5		8	9	17	3	Low Air
6A	3-2	(5.5)	1600	27	197	224	262	
6B	3-2	(5.5)	1600	29	218	247	262	
6F	3-2	(5.5)	1600	42	262	304	255	
7A	3-4	4.8	910	25	14	39	10	
7B	3-4	4.8	910	21	10	31	5	
7E	3-4	5.0	910	26	10	36	4	

[a] Location refers to boiler number and locations marked on Figure 3.

[b] Concentration of the sampled gas.

An indication of the manner in which SO_3 and total sulfate (SO_3 + SO_4) concentrations change as the flue gas moves through the furnace can be obtained by plotting concentration vs. flue gas temperature, as is done in Figure 4. This clearly shows that the highest observed SO_3 concentrations occur closest to the main furnace combustion zone. Instances of silica catalyzing the oxidation of SO_2 at temperatures above 1100°F have been observed elsewhere. While this may have contributed to measured SO_3 in the superheat, a test without the quartz wool plug showed the same SO_3 as the previous test. SO_3 concentrations tend to decrease or remain constant downstream of the furnace section of the boiler.

An apparent increase in total sulfates between the economizer and the air heater exit may be real or a result of insufficient sampling in the economizer area. Much of the data scatter can be attributed to variations in furnace excess air levels which, as noted earlier, are not easy to delineate on a day-to-day basis. Tests 4 and 5 of Table 1 were run during a single shift and show the potential variation in SO_3 due to changes in excess air levels.

Within the operating range of these units, a variation in SO_3 emissions of roughly 3/1 can be achieved with changes in excess air level. This suggests that in using techniques such as low excess air to control SO_3, it is important to control air to the combustion zone, and that control of air leakage in the convective passes is less important.

It is reasonable to expect that some sulfur oxides accumulate on boiler tube surfaces in the process of scale formation. These deposits are removed periodically by sootblowers. No sootblowing operations were conducted during a test, so this accumulative material would not have added to the filtered substances. Thus, a decrease in SO_4, and perhaps SO_3, can be attributed to accumulation, while an increase reflects additional formation.

Magnesium concentrations tend generally to decrease as the gases move through the convective section of the boiler. This may be attributed to accumulation on the tubes which is the purpose of the additive. An anomaly in the data occurred during Test No. 6. It appears likely that the additive pump was improperly set during this period of time. This could explain the magnesium but not the simultaneous large sulfate measurements. Reviewing all the data and remembering that the precision of measurement for Mg is roughly 5 ppm, one notes that sulfate levels are seldom significantly below magnesium levels. Figure 5 shows an apparent correlation between Mg and SO_4. All the SO_4 could be magnesium in the form of sulfate, but it cannot be determined here whether $MgSO_4$ formation occurred

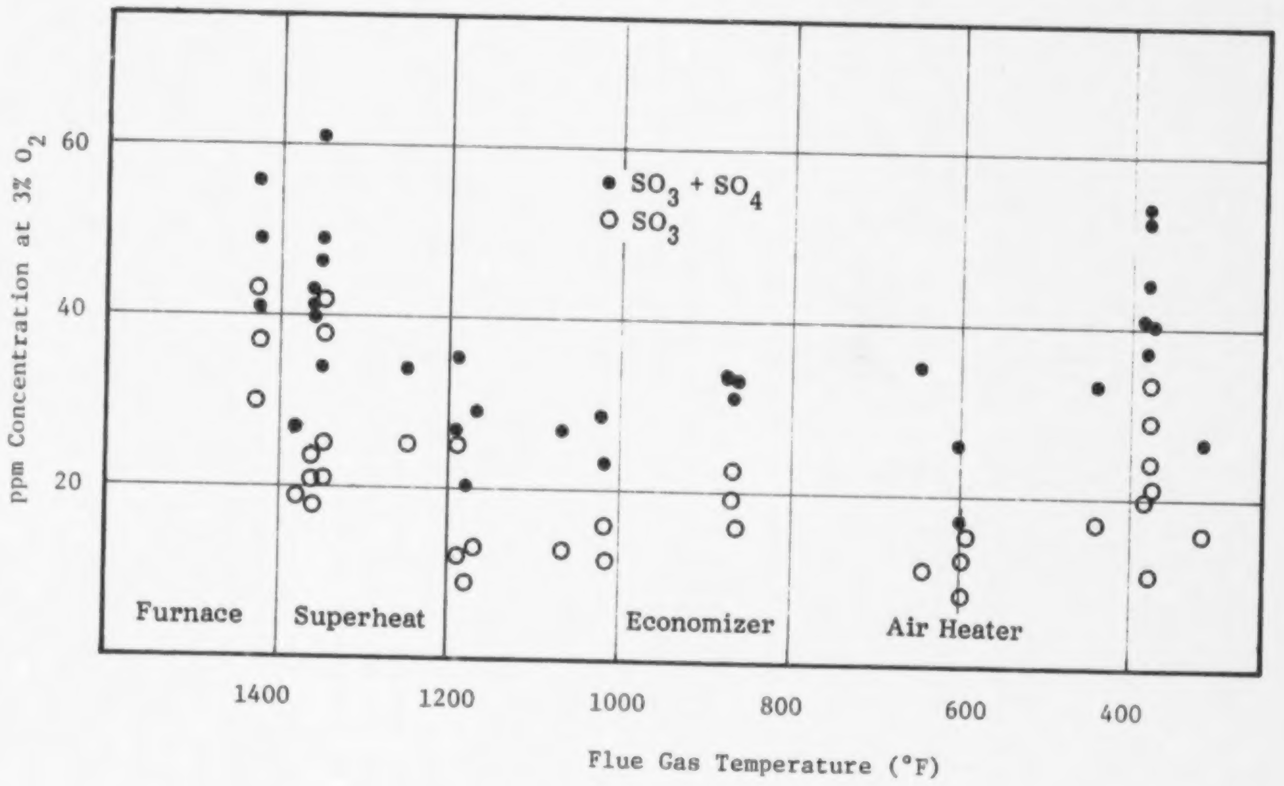

Figure 4. SO_3 and SO_4 data for boiler no. 2.

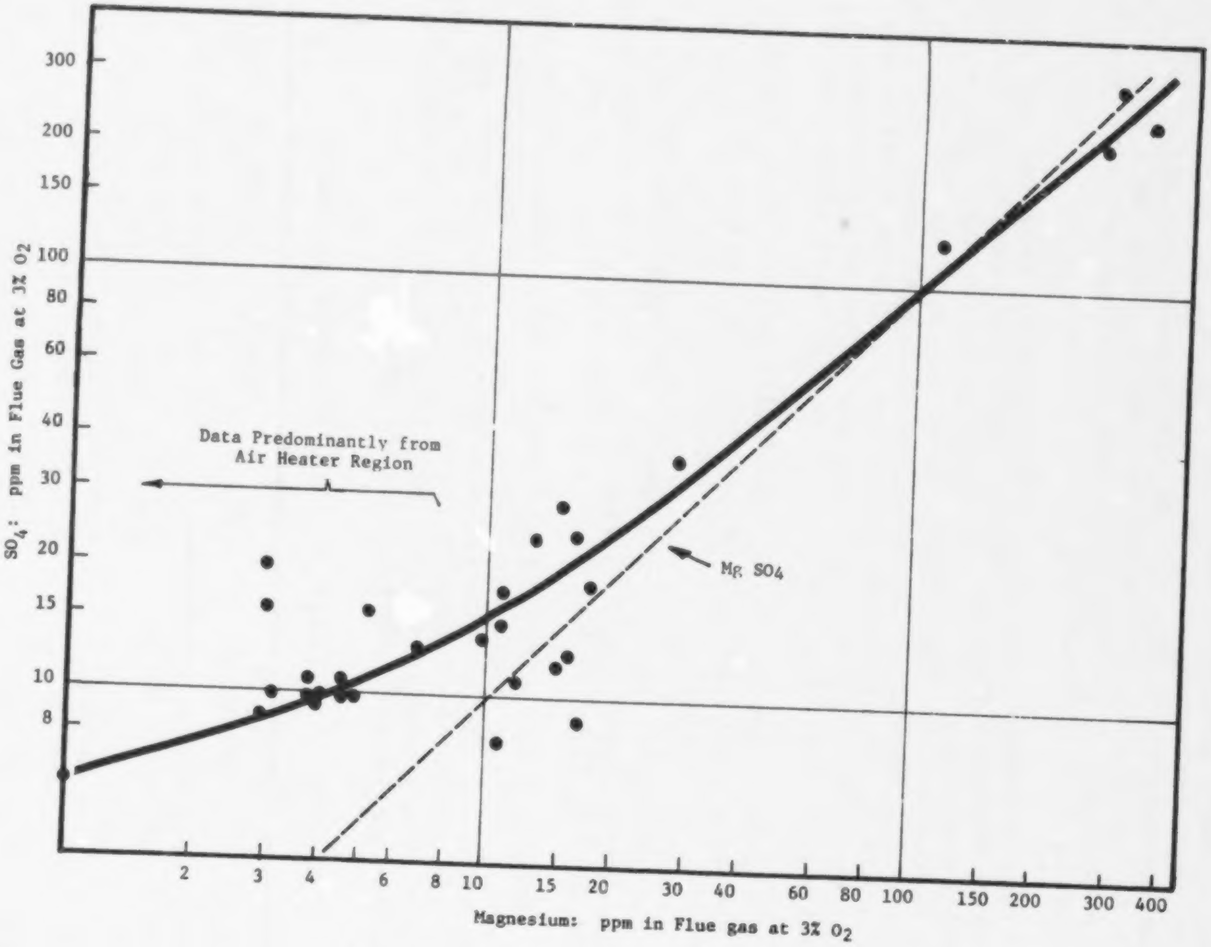

Figure 5. Correlation of magnesium and sulfates on quartz filter.

in the flue gas or as those gases were drawn through a filter coated (after a short period of testing) with MgO. In either case, one is led to the conclusion that the presence of magnesium oxides leads to the conversion of SO_2 to SO_4 in amounts equivalent on a molar basis to the amount of magnesium. While these data may condemn the test procedure, they also call into question how effectively Mg or MgO reacts with gaseous SO_3.

Test 3 exemplifies data which suggest that the MgO additive may have been responsible for a small suppression in the gas phase formation of SO_3. If in fact this is occurring, this and other data indicate that the effect is no larger than 30% of the zero additive SO_3 level. This makes no statement about the effect of fuel additive on catalytic processes in the convective section. Since the tubes of these boilers are permanently influenced by the additive, the SO_3/SO_4 levels with no additive cannot be determined.

Boilers 2 and 3 are equipped with tubular air heaters, which are known to experience difficulties with corrosion and plugging. However, the typical exit air temperatures are high (350°F), and the data here give no indication of diminished SO_3 levels at the air heater exit. Either the amount of condensation is low or the condensation occurs during operating conditions different from those during the testing (i.e., very low load).

Boiler 5 has a rotary air heater with temperatures much lower than the smaller boilers. Table 2 lists the measurements made on both sides of the air heater and at the precipitator exit. These data are substantially more repeatable than the data on the smaller boilers due probably to more predictable boiler operation. A coherent pattern is clearly established.

Table 2. SO_3/SO_4 Data on Unit 5

Test	Location	O_2 (%)	Temp. (°F)	ppm by Vol @ 3% O_2			
				SO_3	SO_4	Total	Mg
1A	Precip. Outl.	4.6	320	2.0	10	12	3
1D	" "	5.3	285	6.6	11	17	4
2A	AH Out	6.2	310	4.1	29	33	15
2E	AH In	5.7	695	20	12	32	15
3A	AH In	4.9	725	23	10	33	5
4A	AH In	3.4	700	18	16	34	5
4D	AH In	5.0	700	23	11	34	5

As the flue gases pass through the air heater, the SO_3 level is diminished by about 15 ppm. Although the data are limited, this corresponds to a 15 ppm increase in SO_4 and suggests that the air heater is condensing the gaseous SO_3 to form acid. This is not inconceivable, given the relatively low exit gas temperatures and known corrosion problems on this unit. When the gases leave the precipitator, the SO_4 and total sulfates are reduced. A precipitator is capable of collecting an acid mist, and it appears that much of the mist created by the air heater is being collected by the precipitator. A final piece of data is that the ash from the precipitator is almost 50% sulfate by chemical analysis. Given the typical fuel ash levels of 0.1% and 15 ppm of collected sulfate in the precipitator, a mass balance suggests that an ash with 50% sulfate should be collected in the precipitator.

The cohesiveness of the data in this case suggests that the test method has considerable value and that much of the scatter observed in other situations is a real variation in the emissions.

CONCLUSIONS

The controlled condensation technique for measuring SO_3 concentration appears to yield rapid and consistent results during field use. Measurement of SO_4 levels by quartz wool in-stack filtration may suffer from interference by magnesium oxide.

Measurements in the higher temperature regions of the furnace are practical and useful for delineating formation regions and mechanisms.

SO_3 formation in the furnace section of the boiler is substantial and much greater than the formation by catalytic reactions in cooler sections. However, this conclusion is drawn from a furnace with low superheat temperatures which continuously uses significant quantities of MgO based fuel additive.

The use of low excess air to minimize SO_3 formation is effective on boilers with casing leaks and substantial amounts of O_2 present in the convective passes and the air heater.

MgO based fuel additives have relatively little effect on flame zone SO_3 formation.

Measurement of Sulfur Oxides from Coal-Fired Utility and Industrial Boilers

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ABSTRACT

The Source Assessment Program sponsored by IERL/EPA under contract 68-02-1874 involves the characterization of a wide range of pollutant emissions for selected industries in the United States. As part of this program, emissions, including those of sulfur oxides and particulate sulfates, were measured for industrial and utility dry bottom boilers firing pulverized bituminous coals. One typical source in each of the two categories was sampled before and after the electrostatic precipitator.

Sulfur emissions from these sources were sampled using a modified EPA Method 8 train in which a filter was inserted between the probe and the first impinger to collect particulate sulfates. Samples for sulfur dioxide, sulfur trioxide, and particulate sulfate analyses were collected simultaneously by maintaining an isokinetic sample flow.

The study results will be compared with the sulfur balance for each system and with the published emission factors. In the case of the utility boiler, the results will be compared with data obtained by a continuous in-stack monitor. Analytical results obtained by on-site titrations will be compared with values measured in the laboratory. Differences in the concentration of sulfur oxides observed before and after the electrostatic precipitator at the industrial site will also be discussed.

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Monsanto Research Corporation, under EPA contract No. 68-02-1874 (Source Assessment), has the responsibility of characterizing the air emissions, wastewater effluents, and solid wastes discharged from selected sources and assessing their environmental impact. This paper describes the measurement of sulfur oxide (SO_x) emissions at two sites typical of two of the source types under study: industrial and utility dry bottom boilers firing pulverized bituminous coal. The results presented here represent only a small part of the extensive sampling effort performed at both sites. The primary objective of the Source Assessment program is to provide the EPA with sufficient information to decide whether emissions reduction is necessary. Meeting this objective involves the characterization of a wide range of pollutants from a large number of stationary sources in four categories: organic sources, inorganic sources, open sources, and combustion sources. In the combustion area alone, 56 source types have been identified for assessment (1) by MRC and TRW. These are listed in Table 1. The relationship of the source types discussed in this paper with those listed in Table 1 is illustrated in Figures 1 and 2 according to fuel use and SO_x emissions.

These two source types can be briefly defined as all boilers (steam generators) which meet each of the following criteria:

1. The primary fuel is pulverized bituminous coal.
2. The operating temperature of the boiler furnace is kept below the ash fusion temperature so that ash remaining in the furnace can be removed as a dry powder (definition of dry bottom).
3. The product of these boilers (steam) is used for electricity generation for public sale for units in the utility category or is used for process heating, space heating, electricity generation for on-site use, or other miscellaneous uses after being generated at an industrial site in the case of industrial boilers.

While coal used by these source types accounts for only 39% of the fuel used by utilities and 6% of the fuel used in industrial boilers, these sources as defined are responsible for 63% and 34% of the SO_x emissions from all utility and industrial boilers, respectively (1). In addition, the population of these units, particularly in the utility area, is expected to increase significantly over the next decade in response to governmental policies directed toward energy self-sufficiency (2).

Table 1. Stationary Combustion Sources Identified for Assessment (1)

Combustion System	System No.
Electric Generation	
External Combustion	
Coal	
Bituminous	
Pulverized Dry	1
Pulverized Wet	2
Cyclone	3
All Stokers	4
Anthracite	
Pulverized Dry	5
All Stokers	6
Lignite	
Pulverized Dry	7
Pulverized Wet	8
Cyclone	9
All Stokers	10
Petroleum	
Residual Oil	
Tangential Firing	11
All Other	12
Distillate Oil	
Tangential Firing	13
All Other	14
Gas	
Tangential Firing	15
All Other	16
Refuse	17
Internal Combustion	
Petroleum	
Gas	
Internal Combustion/ Gas Turbine	
Petroleum	
Distillate Oil	18
Gas	19
Internal Combustion/ Reciprocating Engine	
Petroleum	
Distillate Oil	20
Gas	21
Industrial	
External Combustion	
Coal	
Bituminous	
Pulverized Dry	22
Pulverized Wet	23
Cyclone	24
All Stokers	25
Anthracite	
All Stokers	26
Lignite	
Spreader Stokers	27
Petroleum	
Residual Oil	
Tangential Firing	28
All Other	29
Distillate Oil	
Tangential Firing	30
All Other	31
Gas	
Tangential Firing	32
All Other	33
Waste	34
Internal Combustion	
Petroleum	
Gas	
Internal Combustion/ Gas Turbine	
Petroleum	
Distillate Oil	35
Gas	
Internal Combustion/ Reciprocating Engine	
Petroleum	
Distillate Oil	37
Gas	38
Commercial/Institutional	
External Combustion	
Coal	
Bituminous	
Pulverized Dry	39
Pulverized Wet	40
All Stokers	41
Anthracite	
All Stokers	42
Lignite	
All Stokers	
Petroleum	
Residual Oil	
Tangential Firing	43
All Other	44
Distillate Oil	
Tangential Firing	45
All Other	46
Gas	
Tangential Firing	47
All Other	48
Refuse	
Internal Combustion	
Petroleum	49
Gas	50
Residential	
External Combustion	
Coal	
Bituminous	51
Anthracite	52
Lignite	53
Petroleum	
Distillate Oil	54
Gas	55
Refuse	
Wood	56

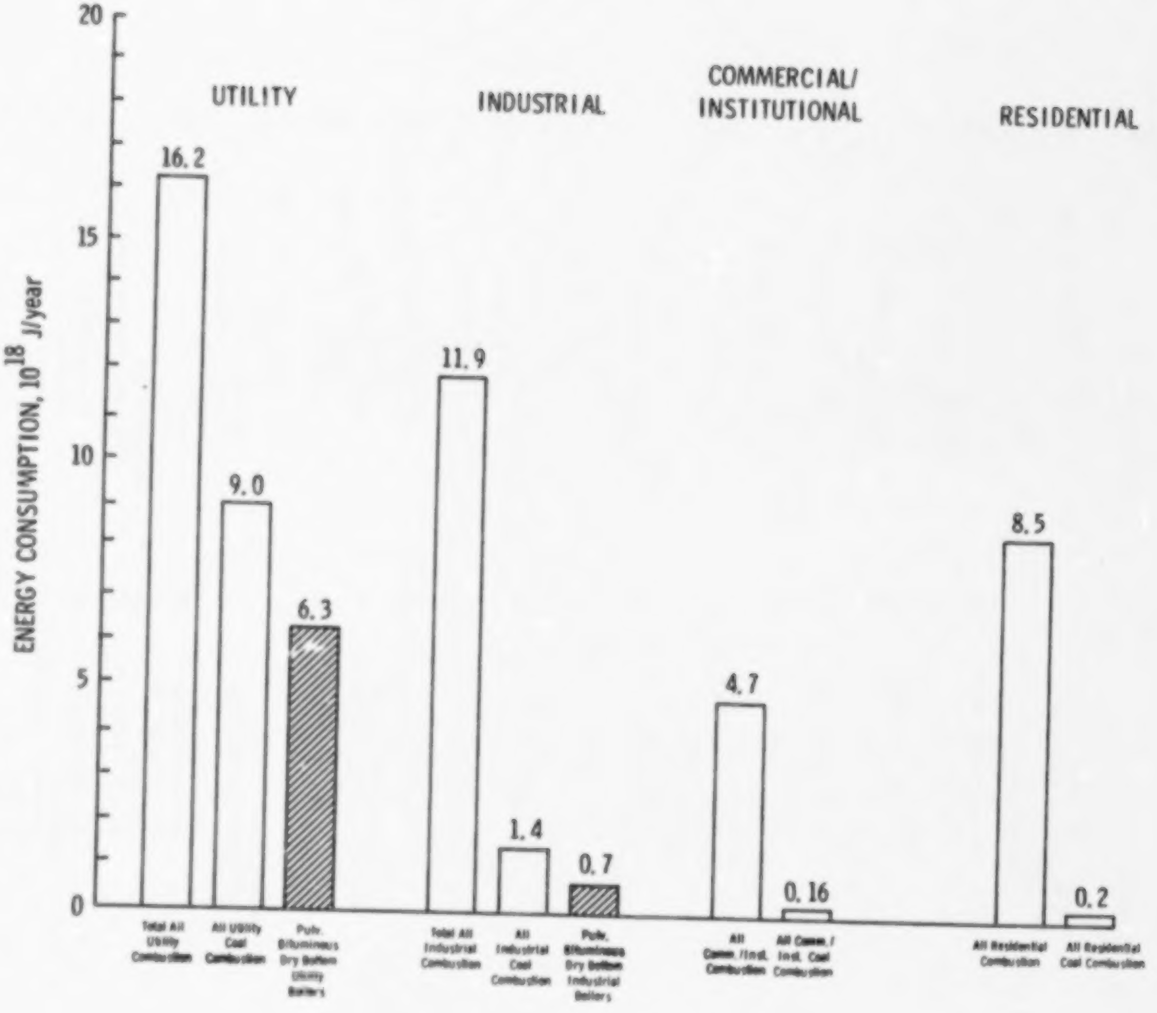

Figure 1. Distribution of energy consumption by source type (1).

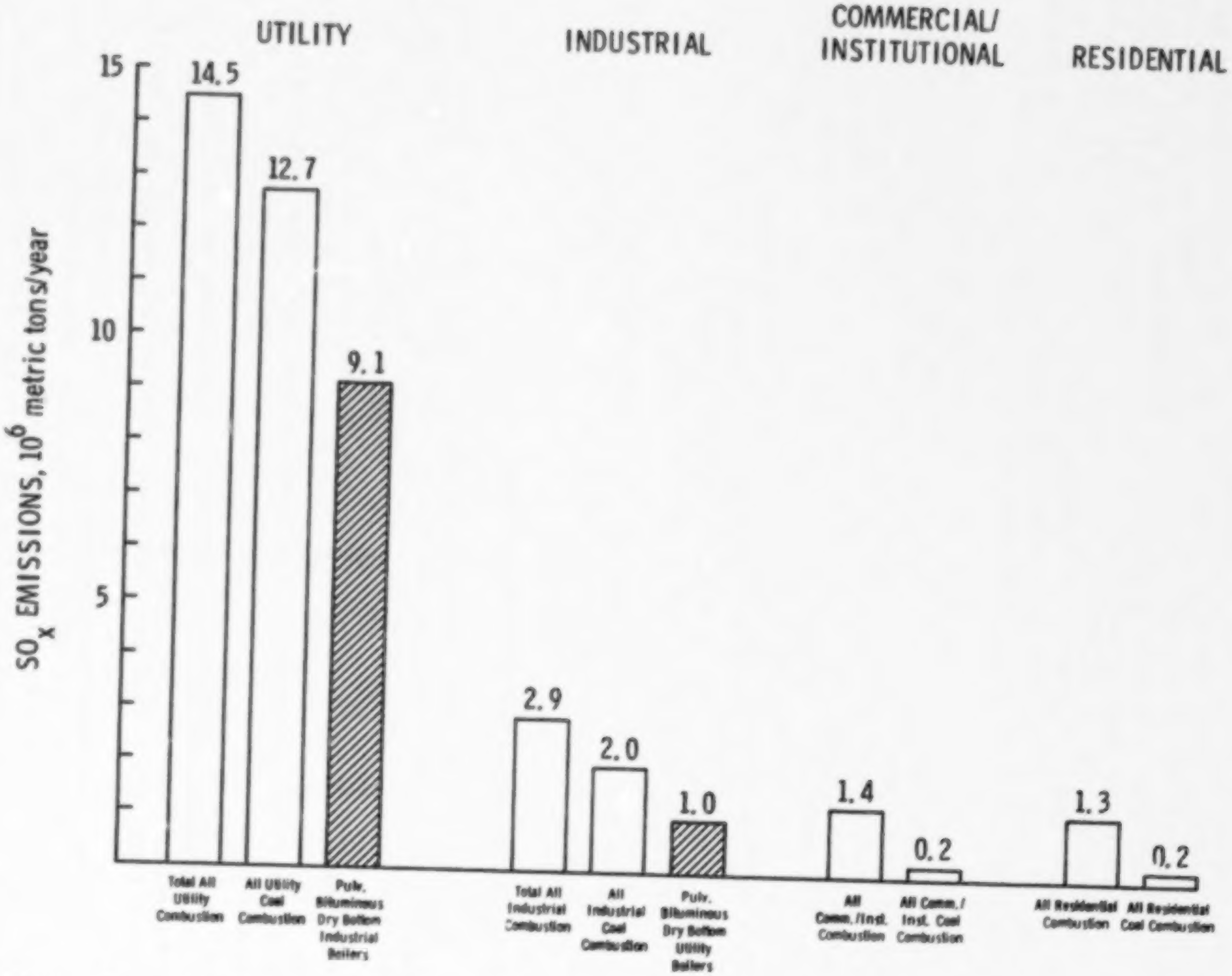

Figure 2. Distribution of SO_x emissions by source type (1).

SITE DESCRIPTION

The industrial boiler selected for testing was a horizontally-fired dry bottom unit with a rated firing capacity of 130 GJ/hr and an output capacity of 45,000 kg of steam/hr. The boiler is fired with a low sulfur (<1.0%) Appalachian bituminous coal and produces steam for process and space heating at an industrial site. Particulate emissions are controlled by a high efficiency (99.0%) electrostatic precipitator (ESP). A schematic of the boiler system showing the path of the flue gas is presented in Figure 3. Air emissions were sampled at the inlet and the outlet of the precipitator.

Emission testing for the utility boiler assessment was conducted on a tangentially-fired dry bottom boiler. The boiler has a design firing capacity of 970 GJ/hr and an output capacity of 590,000 kg of steam/hr at 12.4 MPa and 540°C. Steam produced by this boiler and a similar unit is used to drive a 180 MW electricity generating turbine. Emissions from this boiler are controlled by a mechanical collector (MC) and two ESPs in series. The particulate control system had an overall collection efficiency of 99.97%. Figure 4 illustrates the boiler system showing the path of the flue gases and the sampling points. Sulfur content of the coal burned during sampling ranged from 1.7% to 2.5%.

Results of the analyses of the coals used to fire the industrial and utility boilers tested are listed in Table 2.

SAMPLING AND ANALYTICAL PROCEDURES

Sampling and analytical procedures used for the determination of sulfur dioxide, sulfur trioxide, and particulate sulfates followed the method outlined in the Federal Register for EPA Method 8 (3) with the exception of several modifications. In order to collect a sample for particulate sulfate analysis, an additional glass fiber filter was inserted between the probe and the first impinger. This filter was enclosed in a heated box, and the temperature was maintained at 150°C or above to prevent the collection of any sulfuric acid mist. Leak checks were performed by plugging the inlet to the particulate sulfate filter. Operation of the sampling train was as specified in the Method 8 procedure. This included traversing the flue duct and maintaining isokinetic sampling conditions.

At the conclusion of each run, the particulate sulfate filter was placed in a petri dish and the dish was sealed. The probe and front half of the filter holder were washed with distilled water which was bottled and returned to the lab for sulfate analysis. Remaining portions of the sampling train were washed and bottled following the Method 8 procedures.

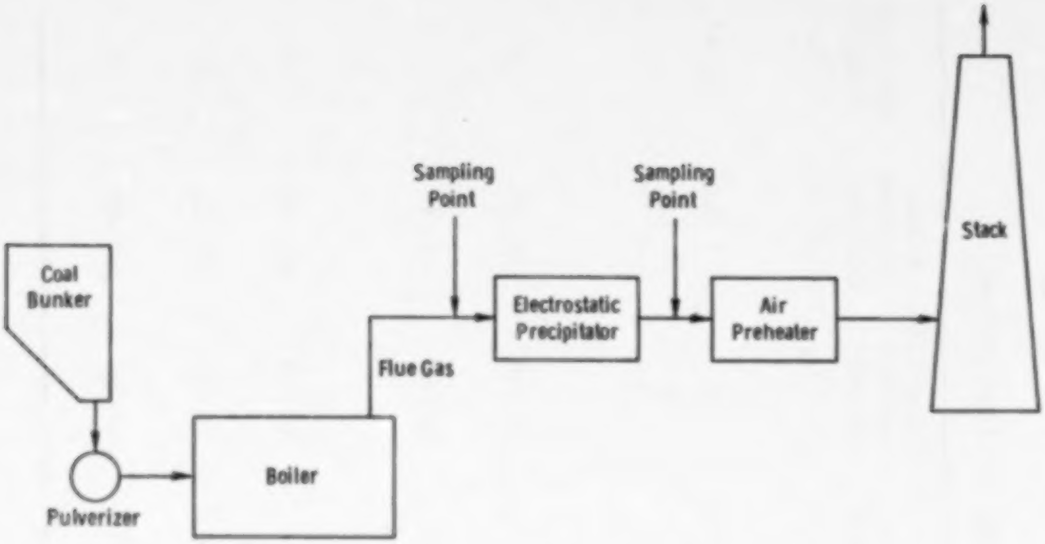
Sampling Point
Sampling Point
Stack
Coal Bunker
Electrostatic Precipitator
Air Preheater
Flue Gas
Boiler
Pulverizer

Figure 3. Schematic of the industrial boiler system.

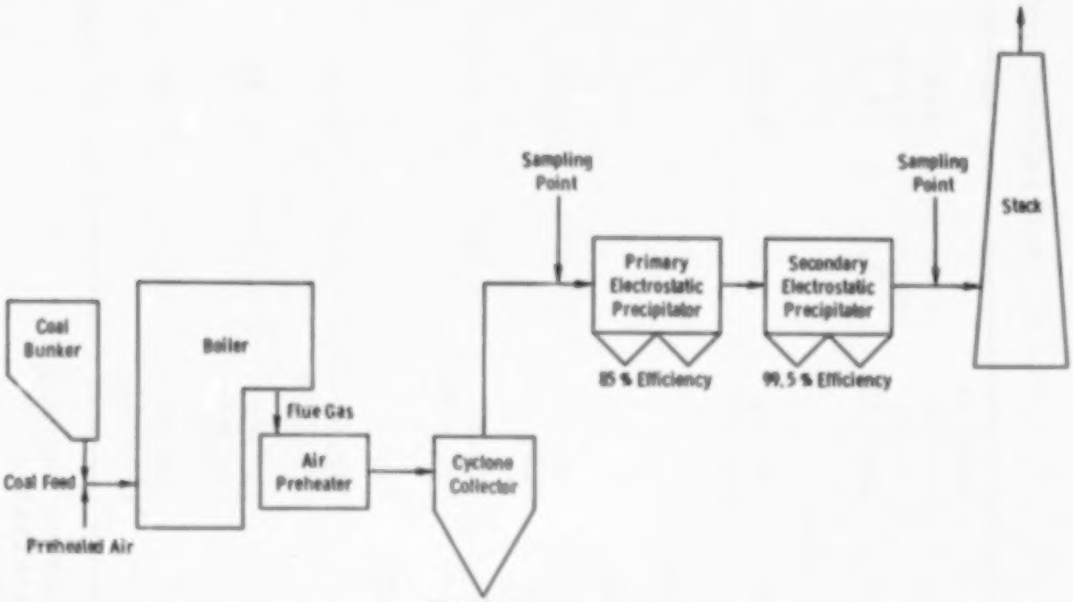
Sampling Point
Sampling Point
Stack
Primary Electrostatic Precipitator
Secondary Electrostatic Precipitator
Coal Bunker
Boiler
85 % Efficiency
99.5 % Efficiency
Flue Gas
Coal Feed
Air Preheater
Cyclone Collector
Preheated Air
65 % Efficiency

Figure 4. Schematic of the utility boiler system.

Table 2. Analysis of Coal Burned at Test Sites

Test run no.	Heating value MJ/kg (Btu/lb)	Moisture content %	Ash content %	Sulfur content %	Volatile matter content %	Fixed carbon content %	Sulfate content %
Industrial site[a]							
All runs	31.38 (13,411)	8.41	8.23	0.91	b	71.59[c]	0.09
Utility site[a]							
MC outlet							
1	28.14 (12,113)	1.62	14.59	2.23	35.39	48.40	b
2	26.57 (11,439)	1.18	23.11	2.45	33.40	42.31	b
ESP outlet							
1	26.02 (11,202)	1.17	19.48	1.81	34.35	45.00	b
2	27.61 (11,886)	1.06	15.89	1.99	35.93	47.12	b
3	26.58 (11,441)	2.25	17.40	1.72	33.99	46.36	b

[a] sampled before pulverizer
[b] no data available
[c] total carbon

Particulate sulfate samples from the industrial site were analyzed for water soluble sulfates. Solid samples collected on the particulate filter were extracted with hot water. The procedure involved: (1) refluxing the filter and particulate matter in 30 ml of water for a minimum of 30 minutes, (2) filtering the hot water through Whatman 41 filter paper, (3) washing the filter twice with 16 ml portions of water, (4) diluting the filtrate and filter washes to 250 ml with isopropanol, and (5) titrating aliquots of the 250 ml sample with barium perchlorate (0.01N $Ba(ClO_4)_2$) using thorin indicator. The combined probe and filter holder wash samples were also diluted with isopropanol to 500 ml or 1000 ml depending on the sample size and titrated with barium perchlorate as described above.

A spectrophotometric procedure was used in the analysis of the utility particulate sulfate samples. The method, developed by Bertolacini and Barney (4) and later refined by Schafer (5), is based on the reaction of sulfate with the barium salt of chloranilic acid (2,5-dichloro- 3,6,-dihydroxy-p-benzoquinone) in isopropanol to produce barium sulfate and chloranilate ion. The absorbance of the chloranilate ion is then measured at 530 mμ and compared to a standard curve.

Sulfur dioxide and sulfur trioxide were determined in both the industrial and utility samples by titration of the impinger solutions with barium perchlorate as specified in Method 8.

RESULTS AND DISCUSSIONS

Results of the emission testing for SO_2, SO_3, and particulate sulfates are presented as emission factors in Table 3. Those from the utility boiler include values from analyses done in the field and in the laboratory. Emission factors calculated with data obtained from an in-stack continuous SO_x monitor at the utility site are shown for comparison. Also in Table 3 the measured emission factors are compared with emission factors calculated using the formula in AP-42 (6). In most cases measured and calculated values show good agreement.

Table 4 compares the mass emission rates of sulfur measured at the sites sampled with the feed rate of sulfur to the boiler, thus providing a partial sulfur mass balance. Emissions of sulfur species measured before the ESPs, with one exception, account for from 92% to 112% of the sulfur entering the boiler. Emissions after the ESP units appear to be somewhat lower, accounting for from 34% to 91% of the sulfur entering the furnace of the industrial boiler and from 88% to 97% for the utility boiler.

Table 3. Emissions of SO_2, SO_3, and Particulate Sulfate from Dry Bottom Industrial and Utility Boilers Burning Pulverized Bituminous Coal

		Emission factors g/kg of coal feed					
Sampling location and test number	Coal sulfur content (%)	Particulate sulfate as SO_4	Sulfur trioxide and sulfuric acid mist as SO_3	Sulfur dioxide as SO_2	AP-42 SO_2 emission factor g/kg	% Agreement of measured values with AP-42	Fraction of SO_x as SO_3 (%)
Industrial site							
Uncontrolled							
Run No. 1	0.91	0.019[a]	0.019	16.8	17.3	97	0.11
Run No. 2	0.91	0.021[a]	0.017	17.4	17.3	101	0.10
Run No. 3	0.91	0.027[a]	0.018	16.9	17.3	98	0.11
Average	0.91	0.023[a]	0.018	17.0	17.3	98	0.11
ESP Outlet							
Run No. 1	0.91	0.024[a]	0.023	14.1	17.3	82	0.16
Run No. 2	0.91	0.008[a]	0.079	6.1	17.3	36	1.3
Run No. 3	0.91	0.025[a]	0.12	9.9	17.3	58	1.2
Run No. 4	0.91	0.003[a]	0.031	16.5	17.3	96	0.19
Average	0.91	0.015[a]	0.063	11.7	17.3	68	0.54
Utility site							
MC Outlet							
Run No. 1							
Field analysis	2.23	b	0.30	49.8	42.4	119	0.6
Lab analysis	2.23	<0.057	0.48	23.0	42.4	55	2.0
Continuous analyzer	2.23	b	b	44.5	42.4	106	b
Run No. 2							
Field analysis	2.45	b	0.17	52.4	46.6	112	0.33
Lab analysis	2.45	<0.059	0.31	48.0	46.6	104	0.64
ESP Outlet							
Run No. 1							
Lab analysis	1.81	0.0006	0.26	31.8	34.4	94	0.81
Continuous analyzer	1.81	b	b	39.2	34.4	113	b
Run No. 2							
Lab analysis	1.99	<0.0002	0.26	34.7	37.8	93	0.74
Continuous analyzer	1.99	b	b	40.2	37.8	106	b
Run No. 3							
Lab analysis	1.72	0.001	0.22	33.1	32.7	102	0.66
Continuous analyzer	1.72	b	b	43.1	32.7	131	b

[a] water soluble sulfates only

[b] no data available

Table 4. Comparison of SO_2, SO_3, and Particulate Sulfate Emission Rates to the Coal Sulfur Feed Rate

Sampling location and test number	Coal feed rate metric tons/hr	Coal sulfur feed rate kg/hr	Sulfur emission rates, kg/hr as sulfur			Total measured sulfur emission rate, kg/hr	% of sulfur accounted for
			SO_4	SO_3	SO_2		
Industrial site							
Uncontrolled							
Run No. 1	3.42	31.1	0.022	0.026	28.7	28.7	92
Run No. 2	3.42	31.1	0.024	0.024	29.7	29.8	96
Run No. 3	3.34	30.4	0.030	0.024	28.2	28.3	93
Average	3.39	30.9	0.026	0.024	28.8	28.9	94
ESP Outlet							
Run No. 1	3.34	30.4	0.026	0.031	23.6	23.7	78
Run No. 2	3.42	31.1	0.009	0.11	10.5	10.6	34
Run No. 3	3.42	31.1	0.028	0.16	17.0	17.2	55
Run No. 4	2.86	26.0	0.003	0.036	23.7	23.7	91
Average	3.26	29.7	0.016	0.082	19.0	19.1	64
Utility site							
MC Outlet							
Run No. 1							
Field analysis	30.5	681	[a]	3.6	760	764	112
Lab analysis	30.5	681	<0.60	5.9	351	358	53
Continuous analyzer	30.5	681	[a]	[a]	678	678	100
Run No. 2							
Field analysis	34.6	847	[a]	2.3	906	909	107
Lab analysis	34.6	847	0.68	4.3	829	833	98
ESP Outlet							
Run No. 1							
Lab analysis	32.7	592	0.007	3.4	520	523	88
Continuous analyzer	32.7	592	[a]	[a]	641	641	108
Run No. 2							
Lab analysis	31.7	631	<0.003	3.3	550	553	88
Continuous analyzer	31.7	631	[a]	[a]	638	638	101
Run No. 3							
Lab analysis	33.5	576	<0.014	2.9	554	557	97
Continuous analyzer	33.5	576	[a]	[a]	721	721	125

[a] no data collected

Concentration of sulfates on particulate emissions are presented in Table 5 to compare the results of each test program on a more uniform basis. Varying particulate collection efficiencies obscure the comparison of particulate sulfate emission factors. Results presented in this table show sulfate concentrations ranging from 0.2 g/kg for uncontrolled emissions to 8.3 g/kg at the ESP outlet, indicating sulfate enrichment on fine particulates.

Table 5. Particulate Sulfate Concentrations

Run No.	Sulfate concentration as g of sulfate/kg of particulate
Industrial site	
Uncontrolled	
Average	0.19
ESP Outlet	
Average	8.3
Utility site	
MC Outlet	
1	<1.5
2	<1.5
ESP Outlet	
1	4.1
2	<1.5
3	8.1

Discussion of Industrial Boiler Results

The percent distribution of sulfur among the emission species measured before and after the ESP is shown in Table 6. Measurements at both locations show >99% of the sulfur in the form of SO_2. This agrees with values predicted for combustion temperatures through

Table 6. Measured Distribution of Sulfur Between SO_2, SO_3, and SO_4

Sulfur Specie	Measured distribution of sulfur, %	
	Before the ESP	After the ESP
SO_2	99.8	99.5
SO_3	0.083	0.45
SO_4	0.090	0.084

equilibrium considerations (7), verifying that concentrations characteristic of high temperatures persist even though SO_3 is the favored species at the stack temperature sampled. This departure from equilibrium is due to a rapid temperature drop at the furnace outlet which quenches the equilibrium reactions. However, these reactions do continue at a greatly reduced rate through gas phase reactions and by catalytic oxidation near metal oxide surfaces. This is shown by the >500% increase in the percentage of sulfur recovered as SO_3 after the ESP. However, it should be noted that reductions in SO_3 emissions were observed after passage through a precipitator in other tests (8).

Particulate sulfates, which have been linked with the concentrations of volatile sulfate forming species (Ca, Mg, Zn, etc.) in the coal, experienced a 30% reduction after the ESP compared to a measured particulate collection efficiency of >98%. This indicates that sulfates were selectively enriched on the smallest particles and may imply that they were forming and condensing in the flue gas stream.

Two aspects of the SO_x emission results were unusual. First, the emission factors determined before the ESP show good precision, but the values measured after the precipitator vary considerably for all three sulfur species. When averaged, the post-ESP measurements are about 30% lower than predicted by AP-42. This is due to an average 30% reduction in the SO_2 emission factor which, according to reports in the literature, should remain relatively constant from the boiler furnace to the stack outlet (7). If the SO_2 measurements are valid, the differences observed before and after the ESP could be due to either an undetected variance in the coal sulfur content or to an interaction of the precipitator with the sulfur species in the flue gas.

Since the SO_x emission testing at the inlet and outlet to the ESP were not done simultaneously, it is difficult to draw conclusions as to the effect of the precipitator. However, this possibility should not be discounted.

A review of the literature on SO_x emissions showed variations in SO_x values measured before and after precipitators but did not reveal any well defined trends. However, a consideration of ESP operating characteristics provides a possible reason for the conversion of SO_2 to SO_3 or SO_4, because the boiler was equipped with a "hot side" ESP. That is, combustion gases flow directly from the furnace to the precipitator and then to heat recovery equipment. Precipitators are used in this configuration for boilers firing low sulfur coal, as is the case for many western coal-fired units. Two potential conversion mechanisms based on the input of energy from the ESP to the combustion gases via the corona discharge (electrical arcing across the electrodes) are postulated. First, arcing in a precipitator may cause localized "hot spots" in which the conversion of SO_2 to SO_3, and/or SO_4 would occur quite rapidly, as the temperature is a dominant rate controlling factor. Since the gases are already hot in comparison to those encountered in an ESP in a conventional configuration, it is plausible that this additional heat input could cause the observed results. The corona discharges also have been shown to produce ozone (O_3) which could readily react with SO_2 to yield SO_3 and O_2. This second mechanism has been presented previously to explain the apparent conversion of N_2 to NO in an ESP (8). The variability of SO_2 emissions observed after the ESP could conceivably be explained by both of these mechanisms, as the degree of arcing is a function of the ash buildup on the electrodes.

Discussion of Utility Boiler Results

Data on SO_x emissions collected at the utility site fall into three categories. Impinger solutions from the two tests after the mechanical collector were titrated in the field and again when returned to the laboratory. Time constraints prevented field titration of the samples collected after the ESP. A continuous gas analyzer was available on site and provided SO_x concentrations at the boiler outlet for all but one run. Test results in Tables 3, 4, and 5 bring out the following points regarding the use of the modified Method 8 train for combustion source sampling:

1. Particulate sulfate emission factors are in relatively close agreement to a previous study conducted on the same source type (9).

2. Sulfates emitted in the flue gas are enriched on the fine particles.

3. Gaseous sulfur emission measurements were in most cases within 10% of the emission factor as calculated from AP-42.

4. The ratio of SO_3 to total gaseous sulfur emissions agrees with values presented in the literature.

These points are discussed below in more detail.

Particulate sulfates collected were, in most cases, below the detection limit of the analytical method, and the detection limit will be used for discussion purposes. The emission factor after the mechanical collector is <0.06 g/kg as compared to a previous study where the sulfate emission factor was determined to be about 0.2 g/kg for a coal-fired unit in the same source category (9). This unit burned a 3.5% sulfur coal and had a mechanical collector of about 50% efficiency as compared to the 2.4% sulfur coal and 65% efficiency of the unit in this study. Correcting for these factors brings the two studies in fairly close agreement. The concentrations of sulfate in particulate were <1.5g/kg in this study versus 5.4 g/kg in the comparative study. When corrected for coal sulfur content, these differ by a factor of 2.

At the mechanical collector outlet, the sulfate species accounts for about 0.2% of the total sulfur emitted, while at the outlet of the ESP it accounts for 0.002%. This corresponds to a removal of about 99%, or about the same as the expected particulate removal efficiency of 99.9%. For the industrial boiler it was shown that sulfate removal in the ESP was 30% versus a particulate removal of 98%, indicating enrichment of sulfates in finer particles. Because the utility boiler ESP train was preceded by a mechanical collector, most of the larger particles had been removed before the ESP; therefore, large differences between sulfate and particulate removal would not be expected.

In Table 5 the concentration of sulfates with respect to particulates is presented for each test run as gram of sulfate per kilogram of particulate. It appears that there is a 3-fold enrichment of sulfates on the very fine particles passing through the ESP train. However, a more sensitive analytical method should be employed to accurately quantify sulfate emissions.

Emissions of SO_3 and sulfuric acid mist were about 0.3 g/kg of coal feed. This amounted to about 0.75% of the gaseous sulfur emissions which is in agreement with previously reported figures of 1.0%-2.0% (10)(11). Laboratory titration of the SO_3 impinger solutions shows about a 70% increase in SO_3 concentration over field titration, indicating that possibly some residual SO_2 remained in the first impinger and was converted to SO_3 in the time between field sampling and laboratory analysis.

Emissions of SO_2 ranged from 30 to 50 grams per kilogram of coal or, in terms of coal sulfur content, about 20S g/kg. As seen in Table 3, field titration of SO_2 impinger solutions resulted in slightly higher SO_2 emission factors than laboratory titration of the same solutions. Laboratory titration of the SO_2 impinger solution of Run No. 1 appears to be in error and cannot be explained at this time. Field titration of Run No. 2 resulted in about a 10% higher emission factor than lab titration. This is in close agreement with an additional run which was not reported because the coal feed rate and coal sulfur content were not obtained by the plant site. Comments by field and laboratory personnel indicate that the titration end point for this method is difficult to detect and may account for some difference in the results. It is the authors' opinion that, whenever possible, field titrations should be performed to obtain more accurate results.

Continuous monitoring of SO_x produced emission factors approximately 20% higher than the modified Method 8 measurement. Both methods were in close agreement with the value predicted by the equation in AP-42.

Table 4 compares the SO_x emission rates, as kg/hr of sulfur, to the sulfur contained in the coal feed also in kg/hr. After reduction of particulate emissions in the MC, the sulfate emissions accounted for almost 0.1% of the coal sulfur. At the ESP outlet, sulfates were reduced to account for about 0.001% of the coal sulfur. About 0.5% of the coal sulfur was emitted as SO_3. Total sulfur emitted, as determined by the modified Method 8 train, ranged from 88% to 112% of the coal sulfur while gaseous sulfur emissions, as determined by the continuous analyzer, accounted for 100% to 125% of the coal sulfur. Other sources have indicated that 90% to 100% of the coal sulfur is emitted in the stack gases (8).

OVERALL CONCLUSIONS AND DISCREPANCIES

The EPA Method 8 procedure for determining SO_2 and SO_3 emissions is not usually employed for characterization of gaseous emissions from combustion sources due to the high particulate loading. Modifying the Method 8 procedure by inserting a filter between the probe and first impinger prevented particulate sulfates from entering the SO_3 impinger and made them available for separate sulfate analysis.

Sampling at both the industrial and utility sites with this method produced gaseous sulfur species emission factors usually within 10% of those calculated by using AP-42. Total sulfur species emissions determined by this method in most cases accounted for 88% to 112% of the sulfur in the feed coal. The degree of variability seen in most of the sulfur species emission factors was minimal for this program in characterizing controlled and uncontrolled emissions.

Emissions of SO_3 from the utility site before the ESP were about an order of magnitude higher than from the industrial site before the ESP. Besides coal sulfur content, differences in distance from the furnace play an important role in SO_3 concentrations. The industrial site sampling was much closer to the boiler outlet, and, therefore, it would be expected to have lower SO_3 concentrations. Emission factors for SO_3 at the ESP outlets were in close agreement. These values may be lower than that expected at the stack outlet. The ratio of SO_3 to the total gaseous sulfur species agreed closely with published values and was about seven times higher for the utility boiler.

Particulate sulfate emission factors are difficult to compare because of the differences in particulate collection efficiencies and the lack of information regarding enrichment of SO_4 on small particles. Comparison of SO_4 concentration on particulate was in fairly close agreement, but it should be recalled that the sulfates measured at the industrial site are water soluble while the utility samples were analyzed for total particulate sulfate. Concentration of sulfates on particulates increased by a factor of 40 after the ESP at the industrial site and by about a factor of 3 at the utility site, showing that enrichment of sulfates on fine particles takes place. Again, because of differences in particulate collection efficiencies and the presence of the mechanical collector at the utility site, these values cannot be compared to each other.

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Sulfur Oxide Measurements of Utility Power Plant Emissions

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ABSTRACT

Sulfur oxide measurements were performed at one oil-fired and two coal-fired power plants as part of the Electric Power Research Institute (EPRI) SURE plume conversion study being conducted by Battelle's Northwest and Columbus Laboratories. The measurements included determination of SO_2, H_2SO_4, and particulate sulfate in the power plant emission streams.

Sulfuric acid sampling was performed primarily with the controlled condensation method. Some measurements were also made with a modified version of EPA Method 6. SO_2 was sampled with impinger trains containing hydrogen peroxide. Sulfate in the collected sulfuric acid and SO_2 samples was determined by barium perchlorate/thorin titration. Particulate samples were collected by in-stack filtration to estimate the sulfate content of the particulate emissions.

The methods that were used for the sulfur oxide measurements will be described, with emphasis on the controlled condensation method for sulfuric acid. Data will be presented on the relative distribution of sulfur species in the power plant emissions, with a comparison of the sulfuric acid measurements by the condensation and modified Method 6 techniques.

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INTRODUCTION

The Electric Power Research Institute (EPRI) has embarked on a major research program known as the Sulfate Regional Experiment (SURE). The objectives of the SURE program are: (1) to characterize the present air quality on a regional basis using the northeastern sector of the United States as the study area, (2) to determine the relationships between gaseous and particulate emissions from fossil-fired utility power plants and ambient concentrations of air pollutants in a regional context, and (3) to develop the capability for predicting and confirming the effect on regional air quality of various electricity production, fuel use, and environmental control scenarios.

As a component of the SURE program, Battelle's Northwest and Columbus Laboratories have been conducting for the past year a study of transformation rates and mechanisms in power plant plumes within the SURE study region. Along with a comprehensive analysis of the power plant plumes by aircraft, concurrent measurements of the source emission characteristics have been conducted. This paper describes the sulfur oxide measurements which have been performed and presents data on the SO_2, H_2SO_4, and particulate sulfate emissions from the three plants which have been studied.

EXPERIMENTAL PROCEDURES

Power Plant Sites

Studies have been performed at three power plants during the first phase of the EPRI program. The plants are Gerald Andrus, Greenville, Mississippi, an oil-fired unit, Breed Power Plant near Sullivan, Indiana, and B. C. Cobb, Muskegon, Michigan. Both the latter are coal-fired facilities. Some of the design and operating characteristics of the three plants are given in Table 1. During the measurements described in this paper, the plants operated under stable full-load conditions, normal operating conditions prevailed, and the units were fired with regular fuel supplies.

Equipment and Procedures

Sulfuric acid measurements were made by the controlled condensation method, and SO_2 was determined by collection in impingers containing hydrogen peroxide. A schematic drawing of the sampling train is shown in Figure 1. A heated Vycor probe equipped with a quartz wool plug at the inlet end was used to extract the flue gas

Table 1. Plant Design and Operating Characteristics

	Andrus	Breed	Cobb
Number of units	1	1	5
Generating capacity (MW)	770	420	Units 1, 2, & 3-60 each Units 4 & 5-155 each
Boiler type	--	Cyclone-fired	Tangentially-fired
Fuel	Fuel oil #6 (w/additive)	Coal	Coal
Fuel source	Domestic, Gulf Coast	Local, strip-mined	Kentucky, deep-mined
Nominal fuel S, %	2.5	3.8	3.5
Flue gas data			
CO_2, %	11	10	8-11
O_2, %	5.5	9.4	7-10
H_2O, %	10	9	7-9
Temperature, F	330	320	285-310
Emission control	Gas recirculation	Cyclones	Electrostatic precipitator
Sampling Location	Stack	Breeching just prior to stack	ESP outlet

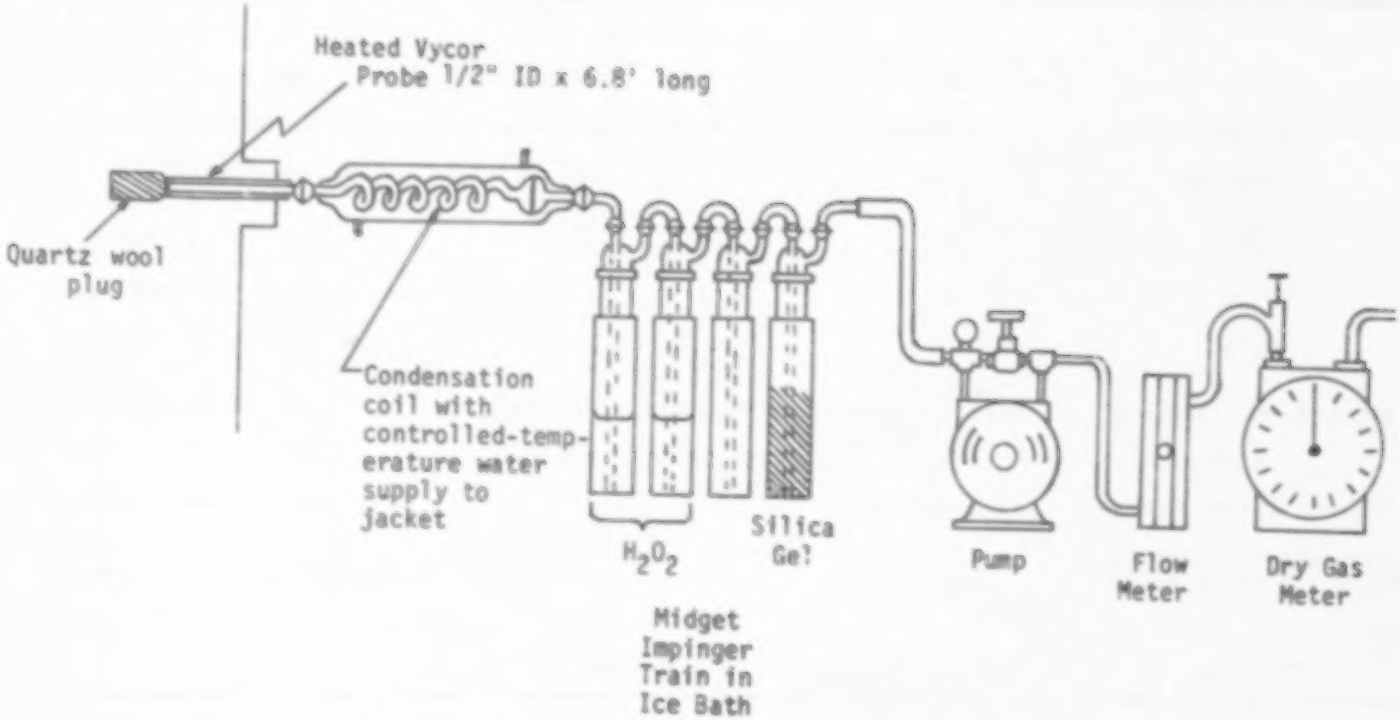
Heated Vycor
Probe 1/2" ID x 6.8' long
Quartz wool
plug
Condensation
coil with
controlled-temp-
erature water
supply to
jacket
H_2O_2
Silica
Gel
Midget
Impinger
Train in
Ice Bath
Pump
Flow
Meter
Dry Gas
Meter

Figure 1. SO_2/H_2SO_4 sampling system.

sample. The probe was preheated at 250°C (482°F) and maintained at this temperature during the sampling period.

Sulfuric acid was collected in the condensation coil immediately following the probe. A detailed drawing of the coil is presented in Figure 2. Water from a constant temperature bath was circulated through the jacket surrounding the coil to maintain the outlet gas temperature at 60°C (140°F) during sampling.

SO_2 in the sample stream was collected in two serially-connected midget impingers, each containing 15 ml of 3% hydrogen peroxide. The remainder of the train consisted of an empty impinger, a moisture trap (silica gel), a pump, and a dry test meter to measure the sample volume.

A sampling rate of 1.5 liters/minute (~0.035 cfm) was used for collection of SO_2 and H_2SO_4. The sampling period for each test was 60 minutes. Following sampling, the sulfuric acid retained by the filter plug and the probe walls was collected by extracting the plug and rinsing the probe with isopropyl alcohol (IPA). The sulfuric acid in the condensation coil was recovered by rinsing with distilled water.

Sulfate analysis of the filter extract/probe washes, coil rinses, and impinger solutions was performed by barium perchlorate/thorin titration using the EPA Method 6 procedure.

The flyash samples for particulate sulfate analysis were collected with an in-stack filter assembly. Pallflex quartz paper which had been acid-washed with 0.1N HCl was used as the filter medium. After collection, the filters were stored under a nitrogen atmosphere until analysis. The determination of sulfate in water and 0.1N HCl extracts of the filter samples was performed by BCL using ion chromatography and by Brigham Young University using calorimetry and ion chromatography.

RESULTS

The results of the H_2SO_4 and SO_2 measurements at the three power plants are presented in Table 2. The sulfuric acid data are based on the sum of the sulfate in the IPA filter extract/probe wash and the coil rinse. A significant quantity of sulfuric acid, typically 20%-30% of the total, was found in the IPA filter/probe washes.

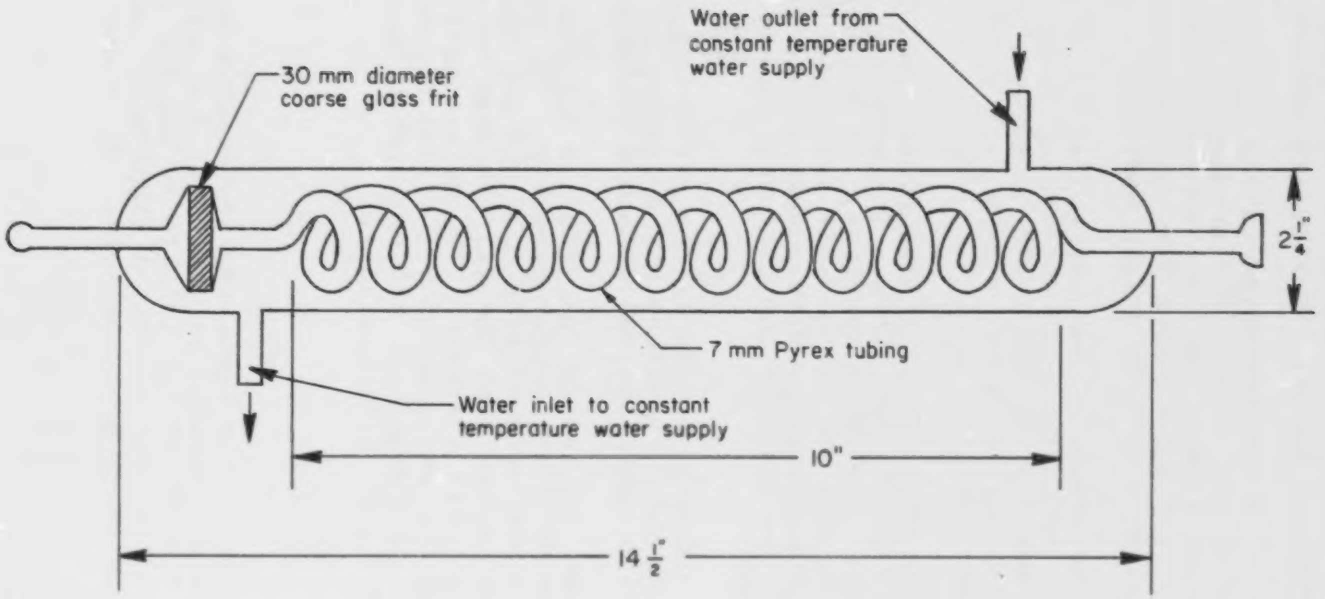
Water outlet from constant temperature water supply
30 mm diameter coarse glass frit
$2\frac{1}{4}''$
7 mm Pyrex tubing
Water inlet to constant temperature water supply
10"
$14\frac{1}{2}''$

Figure 2. Condensation coil used for sulfuric acid collection.

Table 2. Summary of SO_2 and H_2SO_4 Measurements

Site	Date	Concentration in Emissions, ppmv(mg/m^3) H_2SO_4	Concentration in Emissions, ppmv(mg/m^3) SO_2	Ratio, ppm H_2SO_4 / ppm SO_2
Andrus	10/21/77	37.2(149)	1287(3430)	0.029
	10/22/77	45.9(183)	1289(3435)	0.036
Breed	11/4/77	28.9(115)	3324(8858)	0.008
	11/6/77	25.2(101)	3218(8576)	0.008
Cobb				
Unit 1	11/17/77	6.1(24)	2377(6335)	0.003
Unit 2	11/18/77	4.7(19)	2279(6074)	0.002
Unit 3	11/18/77	9.5(38)	2285(6090)	0.004
Unit 5	11/18/77	15.3(61)	2380(6343)	0.006

Measurement of H_2SO_4 emissions at the Andrus and Breed plants was also performed using a modified version of EPA Method 6. In these experiments, considerable quantities of the total sulfate (40%-60%) were found in the water extract of the filter plug and the probe rinse. (Probe temperature during the Method 6 sampling was maintained at 204°C.) Based on total sulfate collected (filter, probe, and IPA impinger), the H_2SO_4 concentrations in the Andrus and Breed emissions were estimated at 53 ppm and 33 ppm, respectively. These values are slightly higher than those obtained by the condensation method; however, this might be due to sulfates which were water-leached from particulates retained by the filter.

The results of the analysis of the flyash leach solutions for sulfate are given in Table 3. The range of values shown for the weight percent of soluble sulfate in the flyash was obtained from analysis of two Andrus samples and four each from the Breed and Cobb plants. A slightly higher concentration of sulfate was observed in the oil flyash acid extract than in the water extract; however, this may result from run-to-run variation. About the same sulfate concentrations were found in the water and acid extracts of the coal flyash samples. Estimates of the particulate sulfate concentrations in the emission are expressed as mg soluble $SO_4^{=}/m^3$.

Table 3. Particulate Sulfate Measurements

Site	Soluble Particulate $SO_4^{=}$, weight %	Estimated $SO_4^{=}$ Emissions mg/m^3 (avg)
Andrus	33 (water) 46 (HCl)	18
Breed	0.5-1.9	54
Cobb	6-8	7

Table 4 presents a summary of the sulfur emission measurements from the three power plants. Estimates of the sulfur distribution in the emissions are given for each plant based on the measurements of the three emission components.

DISCUSSION

Based on the data which have been presented, the following observations can be made relative to sulfur emissions from the oil- and coal-fired power plants.

- The proportion of sulfuric acid in the oil-fired plant emissions was higher than in the coal-fired plant emissions. Sulfuric acid comprised about 3% of the total sulfur emissions from the oil-fired unit versus less than 1% of the emissions from the coal-fired units.
- Sulfuric acid levels in coal-fired emissions varied significantly. About 27 ppm was found in the Breed Plant emissions, while relatively low concentrations of between 5 ppm and 15 ppm were measured in the emissions from the Cobb Power Plant. Both units use coal with about the same sulfur content.
- Sulfuric acid was the major component of primary sulfate emissions (H_2SO_4 + particulate sulfate) from both the oil- and coal-fired power plants. In both types of plant emissions, sulfuric acid accounted for about 90% of the primary sulfate emissions.
- Flyash from the oil-fired plant contained a higher proportion of sulfate than the coal-fired flyash. However, particulate sulfate emission rates from oil-fired plants may not be significantly higher than from coal-fired units.

Finally, the preceding observations should be brought into perspective by pointing out that, by far, SO_2 accounts for the major fraction of the sulfur oxide emissions from power plants. Therefore, transformation of SO_2 in the power plant plume and/or the ambient atmosphere represents a much greater potential for introduction of sulfates into the environment.

Table 4. Summary of Sulfur Emission Measurements

	SO_2[a]			H_2SO_4[a]			Particulate Sulfate	
Site	mg/m^3	ppm	%S	mg/m^3	ppm	%S	mg/m^3	%S
Andrus	3432±19	1288±7	96.6	166±24	42±6	3.1	18±8	0.3
Breed	8717±227	3271±85	98.2	108±12	27±3	1.2	54±12	0.6
Cobb (Unit #5)	6343	2380	99.3	61	15	0.6	7±0.8	0.1

[a] Values are means ± standard deviation where multiple measurements were made.

ACKNOWLEDGMENTS

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Effects of Combustion Modification on SO_3 Formation in Combustion

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ABSTRACT

Primary acid aerosol emissions from the combustion of coal and oil will be reviewed relative to thermodynamic and kinetic considerations. In the case of the former, species distribution will be examined as it relates to typical ash and fuel compositions. Kinetic aspects will be examined relative to catalytic and homogeneous reactions of fly ash constituents under varying fuel/air ratios.

Results of an experimental study on the effect of staged combustion on SO_2 oxidation will be presented. Study results will also corroborate a previous observation regarding enhanced SO_3 formation, for example, that under the same overall fuel/air condition, more SO_3 is produced in staged combustion than in a single-step system. The experiment results suggest that the enhanced SO_3 production may be of more concern as a corrosion-deposit promoter than as a pollutant. The oxidation reactions are dependent on post-flame temperatures, on the extent to which the secondary air mixes with combustion products, and on the oxidation kinetics of CO in the second stage combustion.

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INTRODUCTION

In recent years there has been increasing evidence that sulfates in the atmosphere may be of more concern as a health and environmental hazard than sulfur dioxide. Part of this concern is reflected in the fact that SO_2 levels in the atmosphere have been on the decline, while sulfate levels remain unchanged (1)(2). Historically, it has generally been stated that only about 1%-3% of the sulfur in a fuel is emitted from the combustion system as SO_3 or acid. (In this paper SO_3 and sulfuric acid are considered synonymous, since the presence of water vapor and the reaction of SO_3 with water vapor are so prevalent.) However, since such acid can lead to various sulfates which might be a part of the particulate emissions, it is important to consider these particulates as well as SO_3 as part of the primary acid aerosol. Further, as various combustion modifications (CM) become more widely applied to control NO_x emissions, one must be concerned that these previously held postulations regarding SO_3 and sulfate emissions are valid.

In this paper we present a brief examination of how various CM procedures might influence acid aerosol formation (3) and a more detailed examination of the effect of staged combustion on SO_3 formation (4).

COMBUSTION MODIFICATION

Acid aerosols, in the full sense of the term, include liquid and solid particles containing sulfates, nitrates, and chlorides. In essence, however, this paper is concerned with the sulfates, i.e., SO_3, H_2SO_4, and sulfate salts. The principal reason for this is that the great majority of emissions which may lead to acid aerosols in the atmosphere are sulfur compounds, i.e., sulfuric acid, SO_3, and sulfates, although it is recognized that not all sulfates are acidic. Nitrates have not been observed, nor are they expected thermodynamically in stack particles, but a small amount of nitrate may be formed in the near plume. The sparce information available on HCl or chlorides is in general agreement with basic thermodynamic considerations that the chlorine in fuel will be emitted primarily as gaseous HCl from the stack (5). Evidence indicates that total primary sulfates (i.e., those observed within the first half-mile) can be as high as 20% of total sulfur emissions or as low as 2%.

THERMODYNAMIC CONSIDERATIONS

If we consider the thermodynamic potential for producing acid aerosols, we note that sulfates are by far the most likely acid aerosols to be produced. Figures 1 and 2 illustrate this point. In line with a major interest of this workshop, the characterization of sulfuric acid and sulfate particulate, it is of interest to note in these two figures the prevalance of sulfuric acid emissions from the combustion of oil relative to that from coal. Figures 1 and 2 show this quite clearly. In effect the ash content of oils is too low to compete for the sulfuric acid; conversely the ash content of coals readily converts the acid to sulfate salts.

SPECIFIC EFFECTS OF COMBUSTION MODIFICATION ON ACID AEROSOL

Five combustion modification procedures were considered in this study. These CM procedures are staged combustion, flue gas recirculation, low excess air, low air preheat, and load reduction. Little pilot or field test data exist which directly demonstrate that a particular combustion modification employed to reduce NO and NO_2 will have an effect, good or bad, on primary acid aerosol. The weight of the evidence is that anything which tends to reduce super-equilibrium oxygen atom concentrations in the flame zone will tend to reduce SO_3. On the other hand, if the production of particulate, especially very small particles, is increased, then the production of acid and sulfate solids might be expected to increase through heterogeneous processes. At this time, conclusions regarding the effect of a particular combustion modification on specific equipment must be highly speculative.

Staged Combustion

Archer, et al. (6), report on an investigation of a pilot scale two-scale combustion of a high vanadium residual oil with 2.4% sulfur. Their results demonstrated that SO_3 could be reduced essentially to zero when the first stage was slightly fuel rich. They explained their results by noting from previous work that carbonaceous particles inhibit SO_3 formation, react with SO_3, and physically adsorb it.

Such changes do not mean SO_3 is completely eliminated from the boiler, however. When air is added at the second stage to complete combustion, SO_3 can still be formed. As reported by

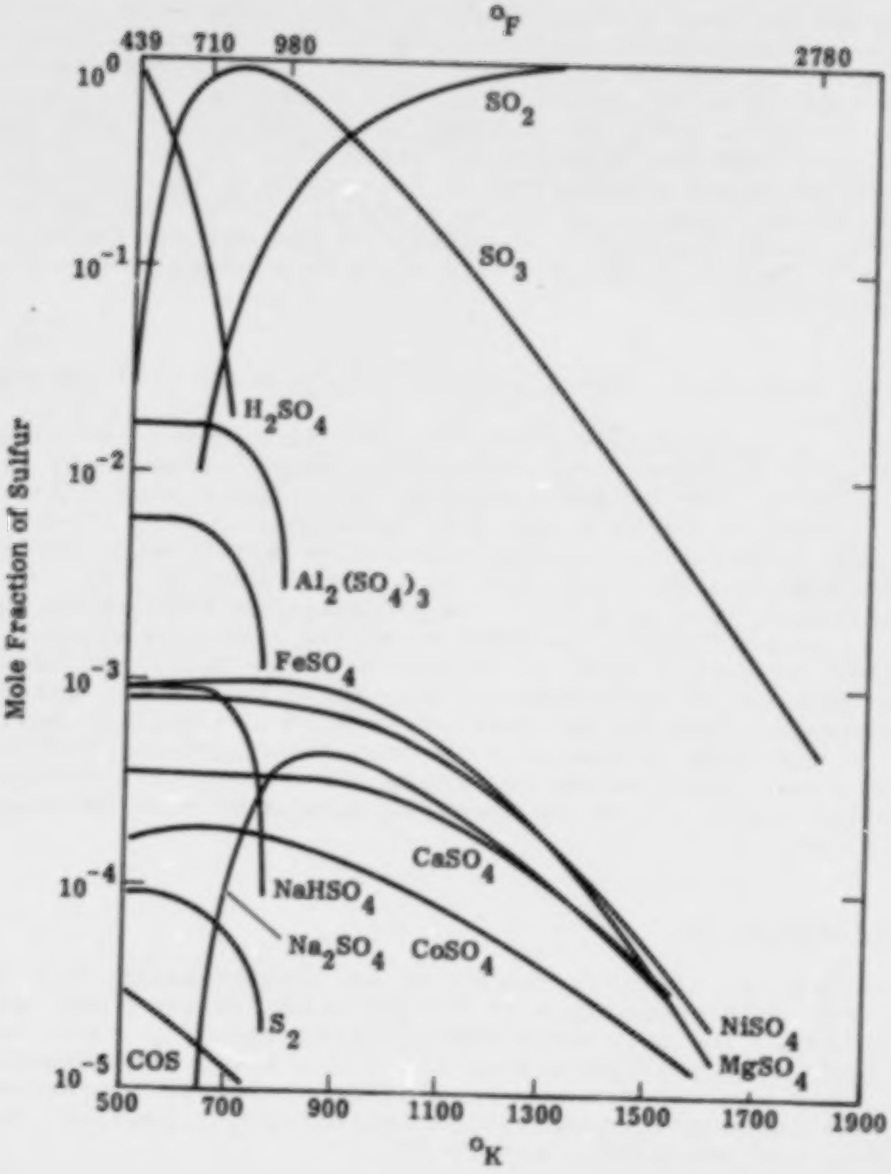

Figure 1. Equilibrium sulfur products for #6 oil combustion with 2% excess air, 2.80% sulfur.

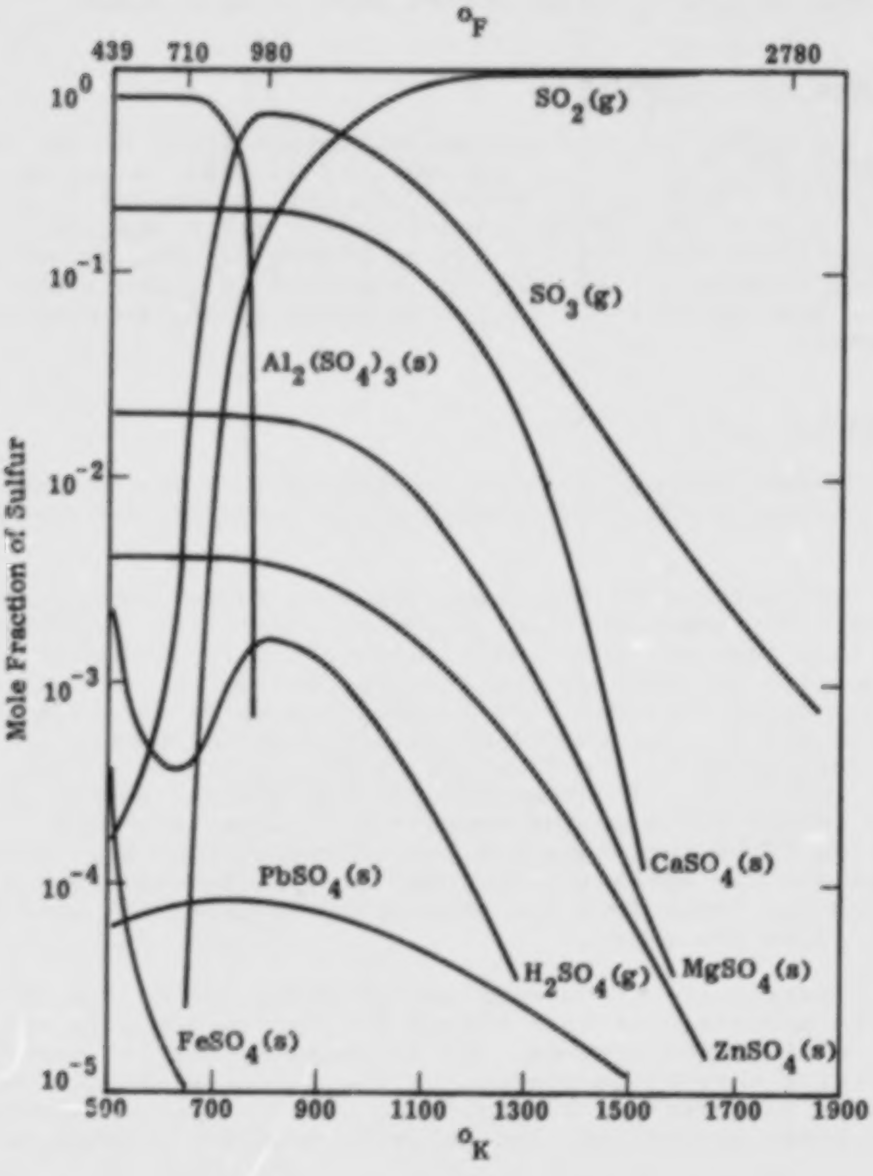

Figure 2. Equilibrium sulfur products for coal combustion with 10% excess air, 3.27% sulfur.

Hedley (7), SO_3 may be produced even in excess of that produced in a single-step combustion process. Hedley's observations are examined in detail in the second half of this paper.

Flue Gas Recirculation

The effect of flue gas recirculation (FGR) on SO_3 formation is not especially clear. Koizumi, et al. (8), studying the combustion of a 2.5% sulfur heavy fuel oil, attempted to relate FGR to SO_3 production and to flame length. Their observations on SO_3 formation are best illustrated by Figure 3. The effect of FGR on acid dewpoint, i.e., SO_3 is inconclusive. One might venture to say that there was a slight decrease in SO_3 as percent FGR was increased.

Low Excess Air

Thermodynamically it is recognized that the percent oxidation of SO_2 to SO_3 is decreased as one reduces the excess air level.

Experience with oil-fired systems, where low excess air operation is most practical at the present time, has demonstrated that this mode of operation minimizes the formation of sulfates in deposits in the high temperature portion of the boiler, reduces the amount of sulfuric acid formed, and eliminates the emission of acid smuts. Successful operation with low excess air requires that the oxygen in the flue gas be maintained at levels below 0.2%. Such operation requires precise control of the fuel-air ratio in all parts of the combustion system to prevent thermal cracking of hydrocarbons and the emission of smoke. Consequently, low excess air operation has been limited to oil-fired systems because the technology for burning pulverized coal with minimal oxygen does not exist.

Glaubitz (9) in Germany was probably one of the first people to take advantage of this effect to control deposits and corrosion in oil-fired systems. By redesigning the oil burners and exercising very close control on the fuel-air ratio, Glaubitz was able to lower excess oxygen to 0.2% for routine operations. Under these conditions, the sulfuric acid was reduced to such

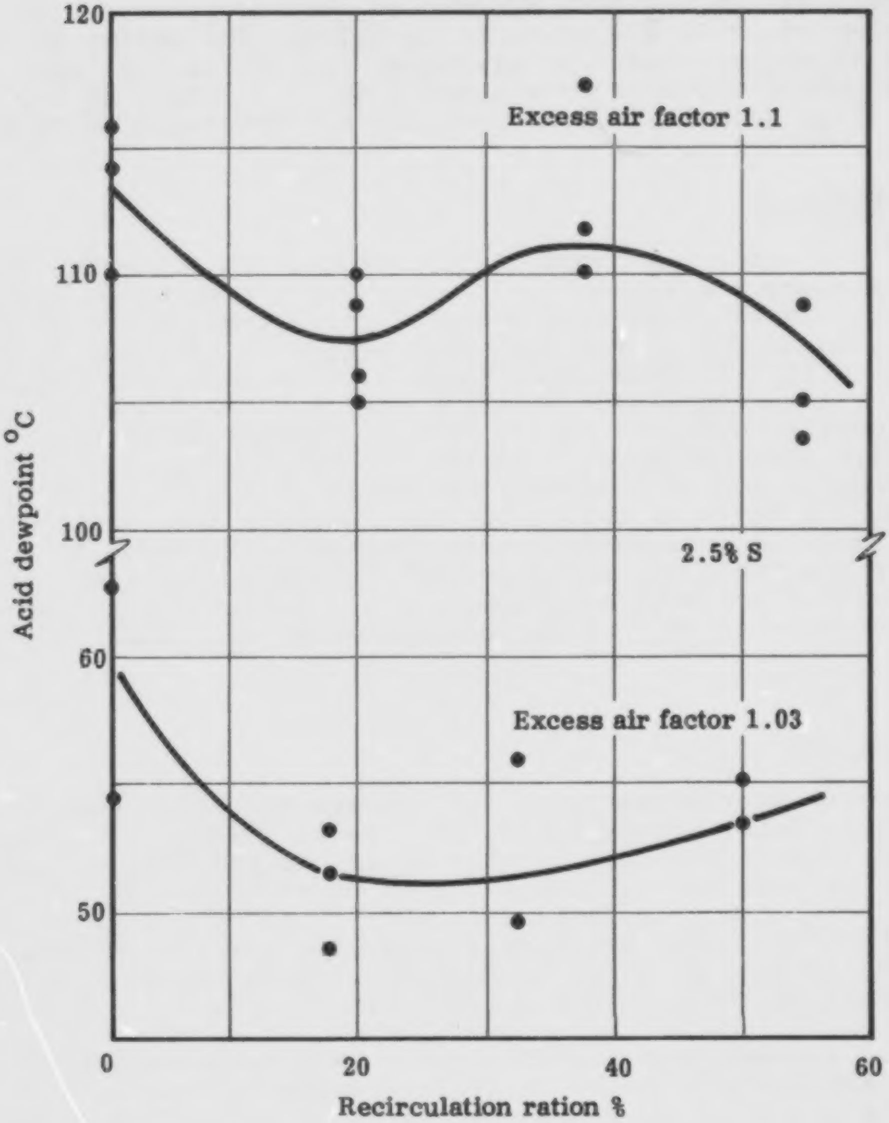

Figure 3. Effect of exhaust gas recirculation ratio on acid dewpoint (8).

an extent that the dewpoint approached that of water. Glaubitz stated that after 12,000 hours of operation, the boiler still did not have to be shut down for cleaning, indicating that the strongly bonded deposits, which build up as a result of the formation of large amounts of sulfates, had not developed in this boiler.

Low Air Preheat

Although there is considerable information regarding the effect of lower air preheat on the SO_3/SO_2 ratio, Glebov (10) points out, "data on the influence of flame temperature on process of formation of SO_3 is very inconsistent." It has been firmly established that in pulverized fuel-fired boilers, the content of SO_3 in the gases decreases with increasing temperature in the furnace. However, Crumley, et al. (11), on the basis of experimental data they obtained..."using kerosene and distillate show an increase in SO_3 to a flame temperature of 1750°C (3182°F) followed by a leveling off. The difference in the results from the two fuels is considerably less than the difference in 2 percent sulfur in the kerosene, and 3 percent in the distillate. At 70 percent excess air with kerosene, about 7 percent of the sulfur was in the form of SO_3; at 28 percent excess air, about 5 percent."

Load Reduction

Based on very meager data, it appears that load reduction has no significant effect on SO_3 emissions. Glebov (10) found no effect of load on SO_3 over a range of 20% to 80% design load in his study of high sulfur, heavy oil in an experimental furnace. In his theoretical computations he also found no change in going from 100% to 70% load, assuming a catalytic activity of deposits equivalent to that produced by Fe_2O_3, but some increase in SO_3 with decreasing load, assuming catalysis by V_2O_5.

Table 1 summarizes the effects of CM procedures on SO_3 formation. Examination of the literature suggests that to date combustion modification procedures have not caused any pronounced effects on acid aerosol formation in general or on SO_3 (sulfate) formation in particular.

The work of Hedley (7), however, did imply that staged combustion might lead to a potential deleterious effect, an increase in SO_3, or, as we refer to it in the remainder of this paper, enhanced SO_3. The second part of this paper discusses a laboratory investigation of staged combustion and its effect on SO_3 formation.

Table 1. Effects of CM on SO_3 Formation

CM	Effect
Staged combustion	Enhanced (increased) SO_3 possible. (Effect may be positive, negative, or nil depending first stage stoichiometry and temperature conditions of second stage.)
Flue gas recirculation	Little direct effect
Low excess air	Decrease in SO_3
Low air preheat	Inconsistent - decrease and increase reported
Load reduction	No effect

STAGED COMBUSTION AND SO_3 FORMATION

The primary basis for examining staged combustion in detail comes about not only from the Hedley study but also from three other studies (12)(13)(14) which indicate that the high CO content in the second-stage firing might readily "pump" oxygen atoms into the second stage and thus promote the homogeneous oxidation of SO_2 in the second stage.

Kinetically the formation of SO_3 is an O-atom process best described by the mechanism (12)(13)

$$SO_2 + O + M = SO_3 + M \quad [1]$$

$$SO_2 + O = SO_3 \quad [2]$$

$$SO_3 + H = SO_2 + OH \quad [3]$$

This mechanism readily accounts for the "excess" or "higher than equilibrium" levels of SO_3 observed by the authors (13), Hedley (7), and others.

Although the oxidation of CO occurs primarily via the OH radical, $CO+OH=CO_2+H$, as Gaydon points out, CO oxidation is accompanied by high levels of oxygen atoms. The Semenov (15) mechanism for the excess O-atoms is

$$CO + O_2 = CO_2^* + O \quad [4]$$

$$CO_2^* + O_2 = CO_2 + 2O. \quad [5]$$

Thus, if one couples the above-stated processes for SO_2 and for CO oxidation, it becomes apparent that conditions may exist where one might expect an increase in SO_3 formation in the second stage of a two-stage combustion process.

Enhanced SO_3 Emissions

At the time of Hedley's studies, no special attention was directed to the use of staged combustion for NO_x control. However, in explaining his evidence on the formation of SO_3 at levels considerably above equilibrium, he describes a one-dimensional controlled mixing experiment and, although this is not presented as such in his paper, he states: "If combustion took place under stoichiometric or fuel-rich conditions then no trioxide formation took place. When less than stoichiometric air was used, the unburnts in the gases consisted solely of carbon monoxide with SO_2 but no SO_3. ***When the remaining excess air was injected into these gases, the maximum amount of SO_3 formed was greater than that formed when this additional air was included with the initial combustion air, the overall excess of air being the same in both cases.***"*

This observation and its potential impact on the effects of staging on SO_3 formation then become closely tied to the effect of CO oxidation kinetics in the second stage production of SO_3. The CO effect is best borne out in Figures 4 and 5 where one notes the highest conversion of SO_2 to SO_3 in sulfur-bearing CO flames (12)(13). When one couples the observations in Figures 4 and 5 with Gaydon's observations of high concentrations of oxygen atoms in CO flames and with the O-atom mechanism for SO_3 formation in combustion, Hedley's statements on the enhancement of SO_3 in staged firing appear quite consistent. Basically then, SO_3 formation is an oxygen atom process, and the question to be addressed is "what is the effect of staging on the oxygen atom concentration?" and its corallary, "what is the effect of staging on SO_3 formation?"

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*Italics signify authors' emphasis.

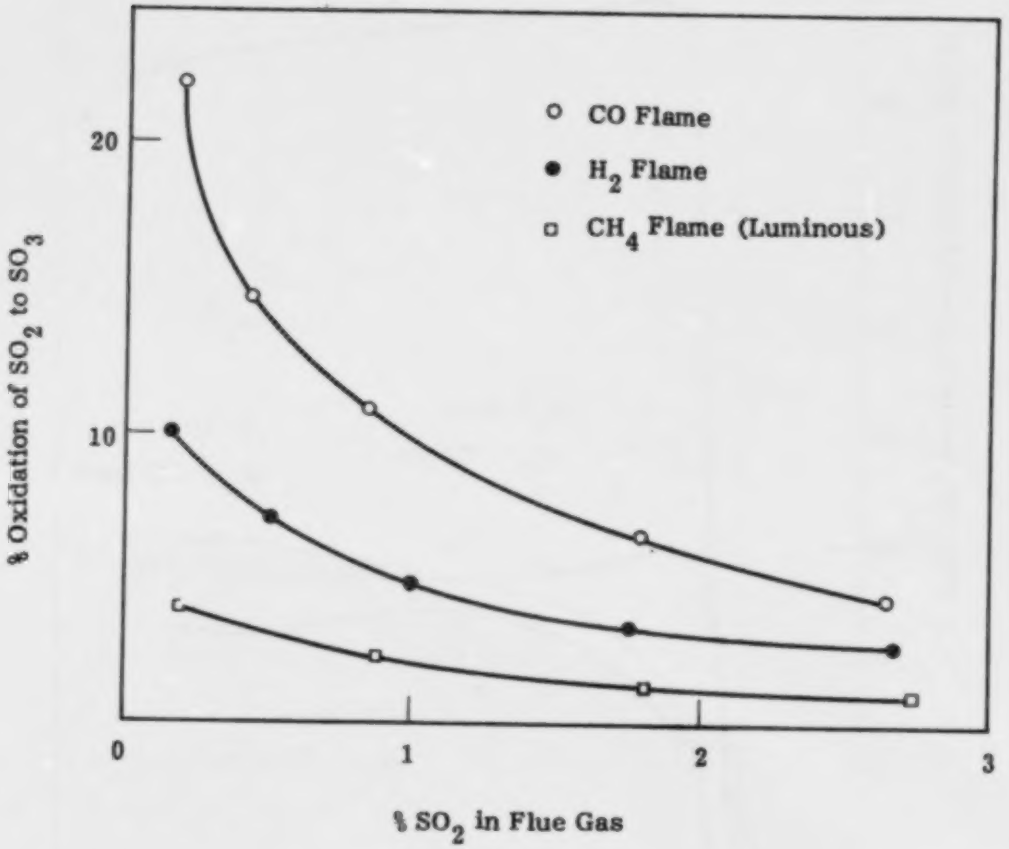

Figure 4. Oxidation of SO_2 in flames from different fuel gases (12).

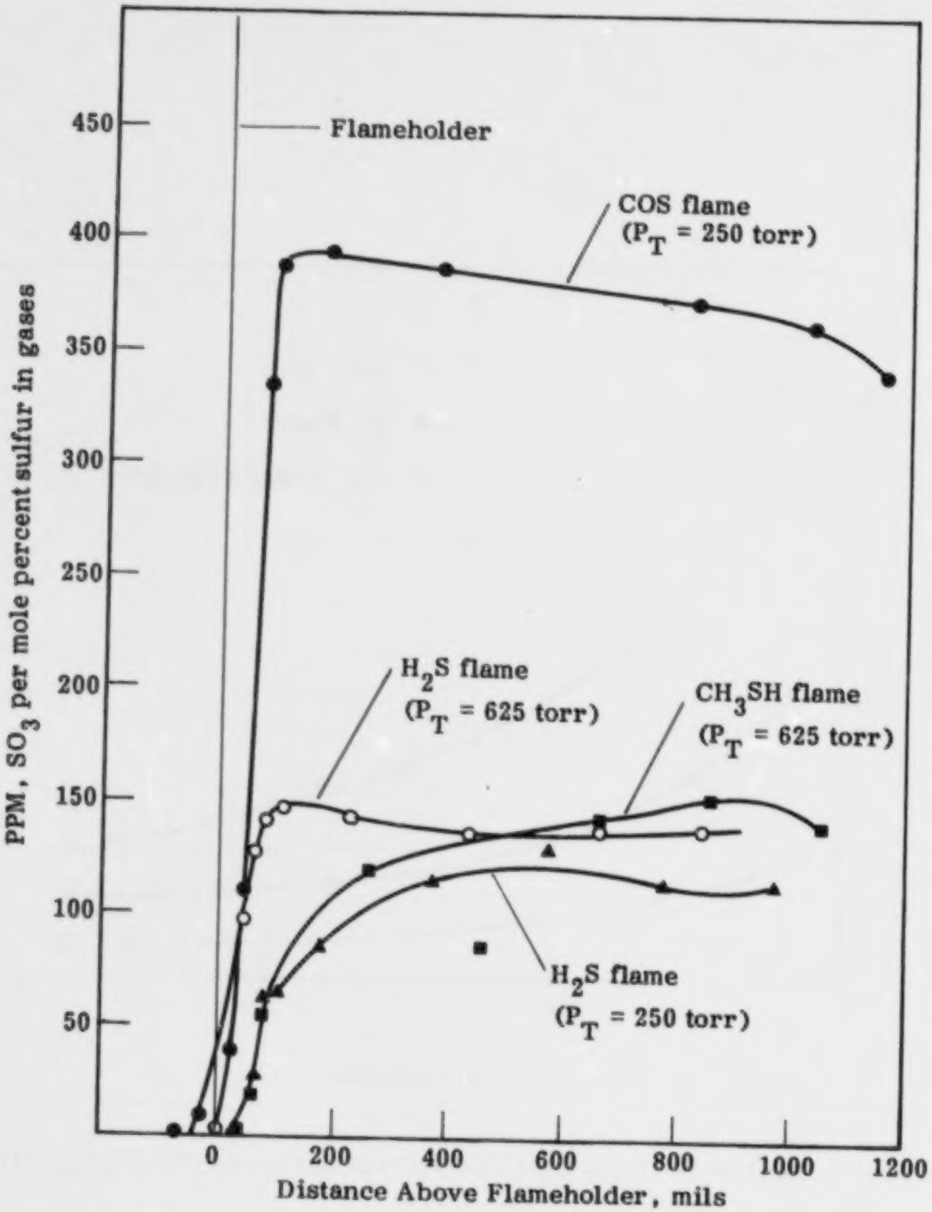

Figure 5. SO_3 profiles in H_2S, COS, and CH_3SH flames (13).

Experimental

A quartz tube burner which allowed one to establish stable methane-H_2S flames within desired fuel-air was used. Two inlets were provided above the flame (first stage) for adding air to complete the combustion process (second stage). SO_3 was then sampled at various positions downstream of the secondary air.

Burner System

The primary burner tube was constructed of quartz (13 mm I.D.) and produced a laminar flow bunsen-type flame (1/D >60). The quartz reaction chamber surrounding the burner tube was 19 mm I.D. This chamber contained several temperature and sampling ports spaced from 3-1/2 to 5-1/2 cm apart in the early postflame zone and increased to about 12-1/2 cm apart in the far postflame zone. These spacings provided appropriate time intervals for collecting the SO_3. The reaction chamber was externally heated (Chromel "A" wiring) to control second stage temperatures. Total chamber length was approximately 76 cm and provided a maximum gas residence time of about 250 msec.

Gas samples were removed at various locations above the flame via a quartz sampling probe. SO_3 was analyzed colorimetrically by the barium chloranilate procedure. CO, CO_2, O_2, and SO_2 were also measured, mainly for purposes of confirming and comparing postflame combustion conditions and sulfur oxide levels with calculated cold gas compositions. Details of the apparatus and analytical techniques are described in Reference 4.

Flame Conditions

Three flame compositions were probed in detail for SO_3 profiles in this study. The compositions were:

Mole Fraction (Cold Cases)

		Two-Stage*	
Gas	Single State ϕ_s = 1.1	1st Stage ϕ_1 = 0.95*	1st Stage ϕ_1 = 0.90*
CH_4	0.087	0.099	0.104
O_2	0.191	0.189	0.188
N_2	0.720	0.710	0.706
H_2O	0.0015	0.0017	0.0017

* In the second stage, ϕ_2 = 1.1; mole fractions were the same as in the single stage firing.

Equivalence ratios, defined as

$$\phi = [Air/Fuel]/[Air/Fuel]\ stoich,$$

are expressed as ϕ_s, ϕ_1, and ϕ_2, i.e., ϕ_s, single stage; ϕ_1, first stage; and ϕ_2, second stage. In all experiments the second stage firing introduced sufficient air that ϕ_2 was comparable to ϕ_s.

Results and Discussions

The staged combustion experiments are summarized in Figures 6, 7, and 8. In essence the data show three distinct effects of staged combustion on SO_3 formation.

Figure 6 shows definite enhancement where ϕ_1 = 0.95. Curves B and C show an absolute increase of some 9% in SO_3 formation compared to Curve A, the single stage process.

Curves B and C in Figure 6 also show the effect of adding the secondary air at two different positions in the postflame gases. Comparison of these two curves shows that altering the distance between the burner head and the introduction of secondary air produced some changes in the shape of SO_3 curves, particularly in the 40-150 msec range. Although maximum SO_3 levels are nearly the same in either of the two-stage modes of firing, the depletion of SO_3 appears to occur more rapidly when the addition of secondary air is delayed several msec (Curve C).

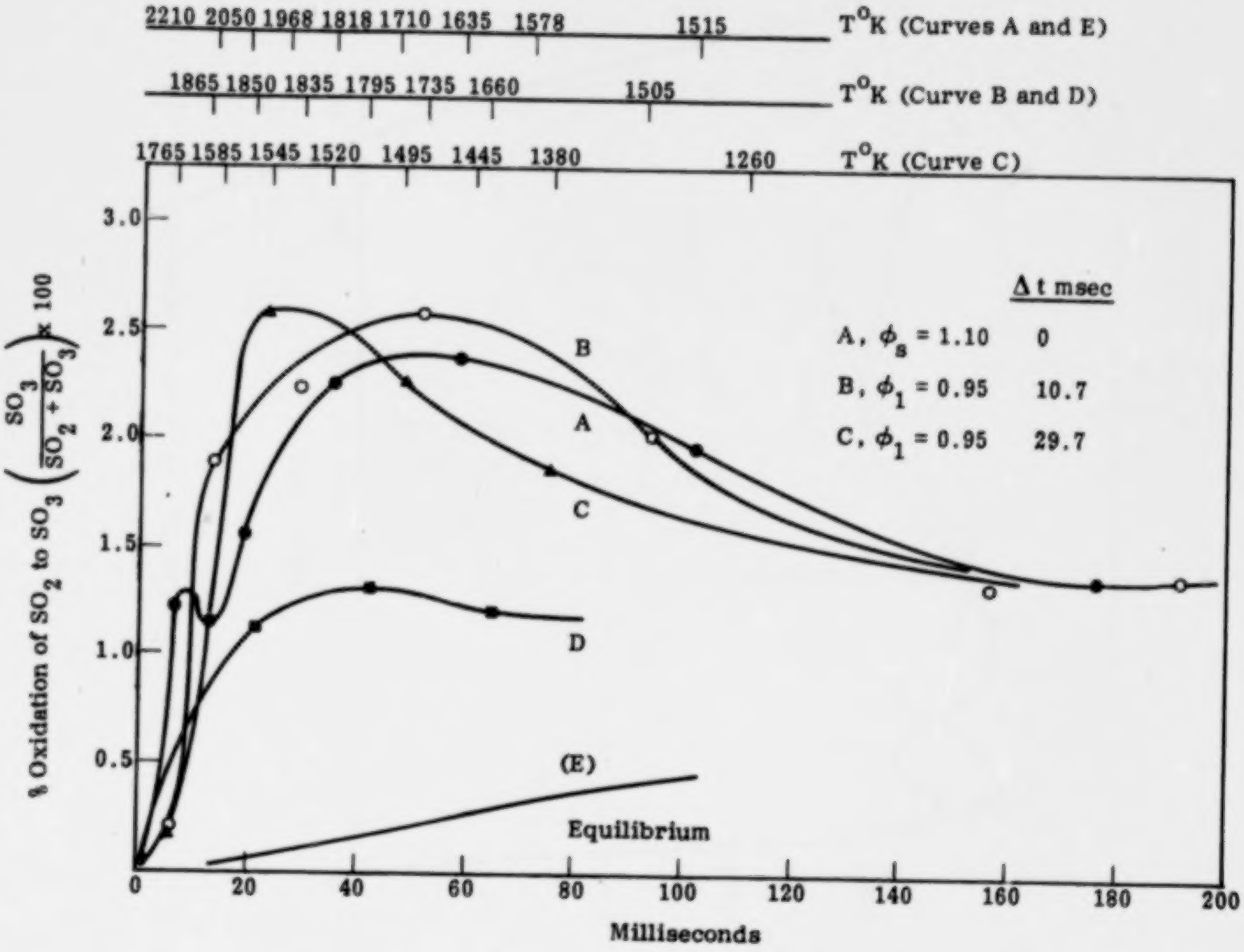

Figure 6. Oxidation of SO_2 in single- and staged-combustion, $\phi_1 = 0.95$.

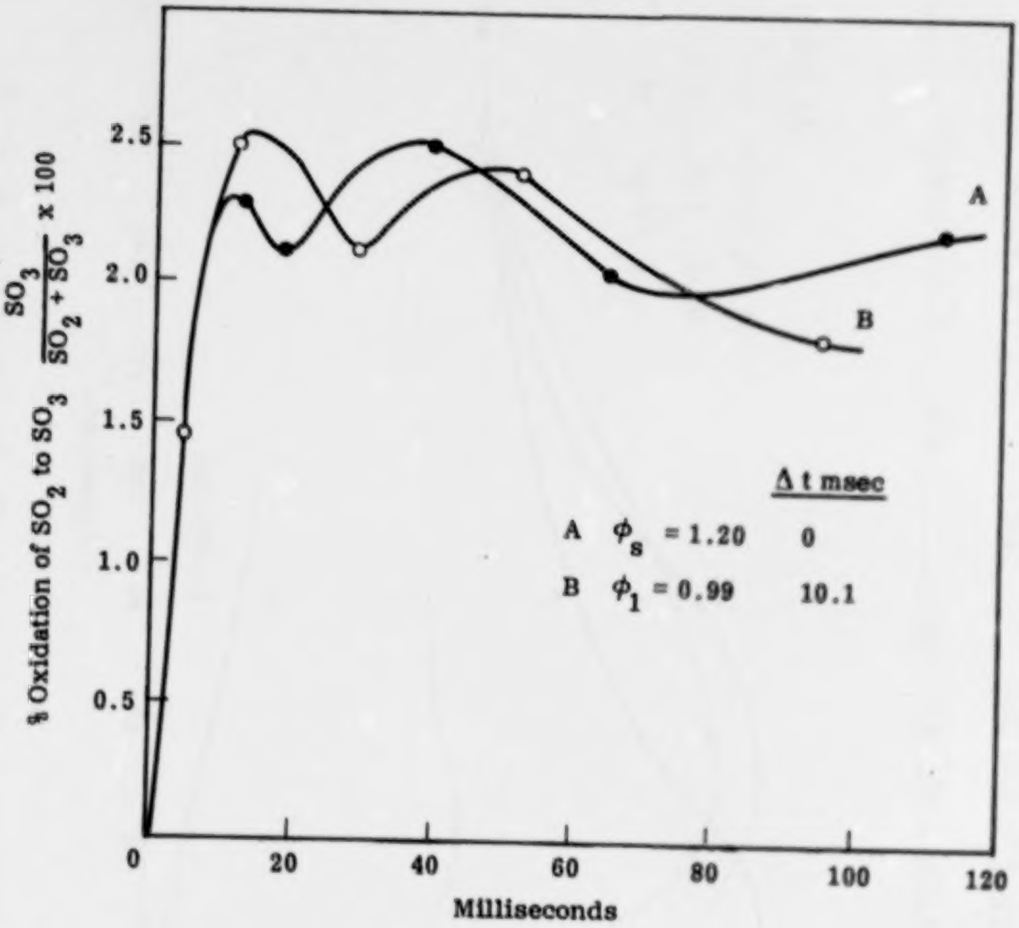

Figure 7. Oxidation of SO_2 in single- and staged-combustion, ϕ_1 = 0.99.

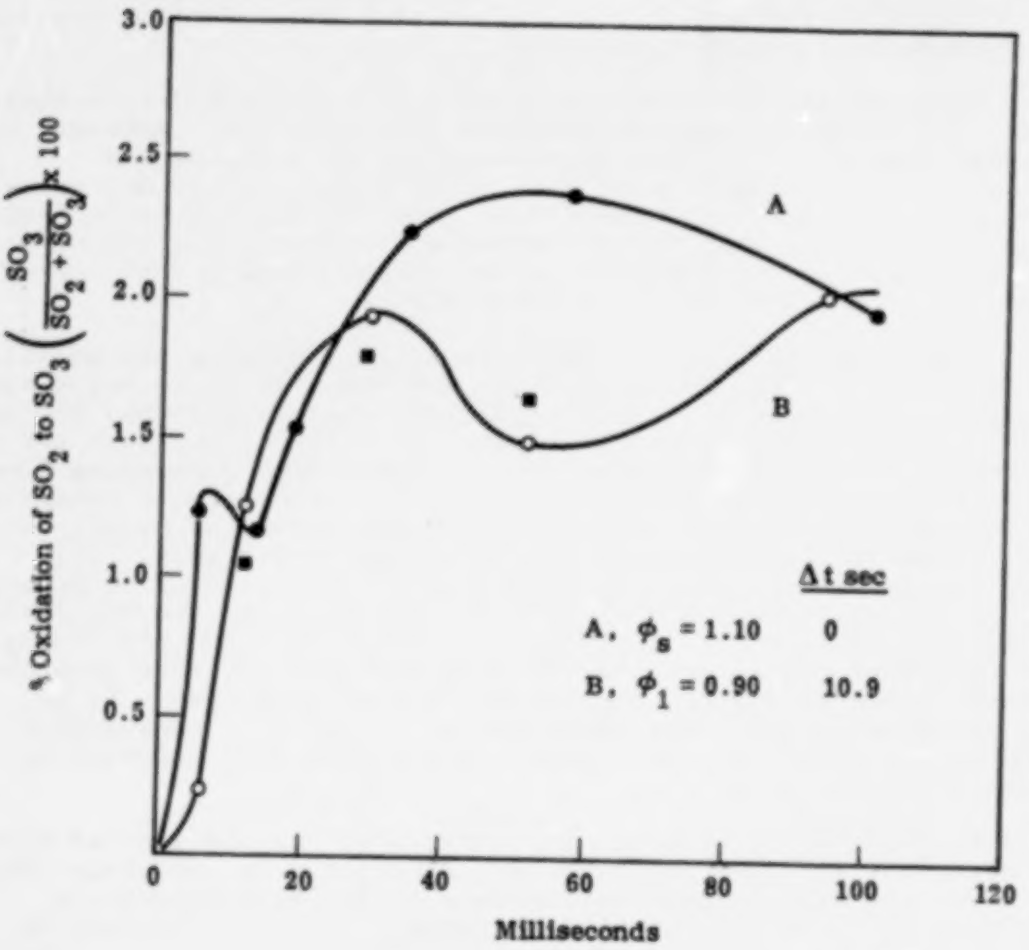

Figure 8. Oxidation of SO_2 in single- and staged-combustion, $\phi_1 = 0.90$.

Figure 7, where ϕ_1 = 0.99, barely sub-stoichiometric, the comparative differences of two-stage versus single stage combustion are negligible.

Figure 8, where ϕ_1 = 0.90, shows that SO_3 formation can also be decreased by staged combustion.

Enhancement--The data presented here confirm Hedley's statement that staged combustion enhances SO_3 formation. However, our results indicate: (1) the effect may not be a pronounced effect, (2) the enhancement is of short duration, the SO_3 appearing to approach steady state conditions about as rapidly as in single-stage combustion, and (3) the enhancement effects and its duration are dependent on the air/fuel ratio of each stage and the delay interval in the addition of secondary air.

Time Delay Effects--It is obvious that delaying the addition of secondary air to the point where the temperature is below that required to produce favorable conditions (mainly O-atoms) for SO_2 oxidation prevents further SO_3 formation. It follows that the formation of SO_3 would, therefore, decrease with decreasing temperature at the secondary air ports. Barrett, et al., have commented to this effect in their examination of the formation of SO_3 in a small combustor using single and two-stage firing modes (16). They concluded from their studies that the addition of secondary air at temperatures below about 950°C would likely produce little or no additional SO_3. In the present study we find that adding the secondary air at about 850°C produced less SO_3 than when the air was added at higher temperature, and no enhancement of SO_3 was observed at the lower temperature. Thus, the "nonreactive temperature limit" may be somewhat lower than that observed by Barrett, et al.

Air/Fuel Ratio Effects--In considering the ultimate effects of different air/fuel ratios on SO_3 production in two-stage combustion, one might expect an increase in SO_3 with decreasing air/fuel ratio in the first-stage firing. This is reasoned on the basis of an increased CO level in the first stage, followed by a greater enhancement of SO_3 from the CO oxidation chemistry. However, temperature effects also influence the chemistry here. As the air/fuel ratio is dropped well below stoichiometric, the temperature of the first stage is decreased. As a consequence, a larger amount of secondary air is needed to restore the second stage to the desired overall equivalence ratio. Further cooling of the gases takes place with a resulting overall reduction in the rate of CO oxidation, a lower O-atom concentration, and hence less SO_3 formation, as observed in comparing the data of Figures 6 and 8.

On the other hand, approaching stoichiometric conditions in the first stage increases the flame temperature to near a maximum, leaving less CO to be oxidized in the second stage. This could, within limits, lead to less SO_3 formation relative to a richer first stage firing. Data from the present flame probings do not show any enhancement in SO_3 formation in a two-stage process at $\phi_1 = 0.99$ (Figure 7).

SO_3 Fluctuation--The data in Figures 6, 7, and 8 show an interesting, as yet unexplainable but repeatable, discontinuity as SO_3 approaches its maximum. The authors have observed similar fluctuations in their microprobing of H_2S flames, which they attributed to the oxidation of SO (17). Interestingly, Hunter's model for SO_3 formation shows a similar fluctuation (18).

Kinetics Analysis

The profiles of Figures 6, 7, and 8 provide a means for analysis of the rate constants for K_1 , K_2, and ratio k_1/k_2. The kinetics analysis is summarized in Table 2. (Additional details on these analysis are presented in Reference 4.)

Table 2. Kinetic Analysis
(T=1685K)

$SO_2 + O + M \quad SO_3 + M$	
$k_1 = 7.4 \times 10^{14}$ cm^6 mole^{-2} sec^{-1}	This study
$k_1 = 1 \times 10^{15}$ cm^6 mole^{-2} sec^{-1}	Reference 19
k_1/k_2	
$k_1/k_2 = 6.6 \times 10^3$ cm^3 mole^{-1}	This study
$k_1/k_2 = 10^4$ cm^3 mole^{-1} (est.)	Reference 19

SUMMARY

It does not appear that combustion modification procedures will severely affect acid aerosols emissions or, more specifically, SO_2 emissions. On the other hand under some conditions, dependent on the fuel/air ratios of the first stage and the temperature of the second stage process, staged combustion can lead to enhanced SO_3, decreased SO_3, or essentially the same SO_3 levels as observed in normal, single stage combustion. This study points out that one must consider the specific conditions existing in the combustion chamber before comparing sulfate emissions from one boiler to another.

This paper is based on two studies carried out at Battelle-Columbus Laboratories under Environmental Protection Agency support, namely Contract No. 68-02-1323 Task 49 and Grant No. R 805330010. The contents of these studies do not necessarily reflect the views and policies of the Environmental Protection Agency.

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Impact of Sulfuric Acid Emissions on Plume Opacity

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ABSTRACT

Concurrent measurements were conducted on plume opacity, stack gas opacity, sulfate, and gross particulate loading in the emissions from coal- and oil-fired power plants. Plume opacity was measured by EPA Method 9 and by Lidar, stack gas opacity by an in-stack transmissometer, sulfates by modified EPA Method 6, and gross particulate loading by EPA Method 5.

Results indicated a significant difference in plume opacity as compared with in-stack opacity in an oil-fired combustion source. The plume opacity was always higher and the difference increased with higher acid emissions and with distance downstream from the stack exit. Plume opacity data on coal-fired sources with particulate but no gas controls were limited to Method 9, and the few measurements available showed considerable scatter compared with in-stack opacity data. No conclusions could be drawn.

Preliminary measurements have been made on a coal-fired power plant with both particulate and gas controls (FGD). The data were not adequate to draw any conclusions. Further studies are under way on high-sulfur coal-fired plants with FGD systems and emissions with pronounced and persistent visible plumes.

INTRODUCTION

Emission standards for opacity and for mass concentration of particulate matter have been established for new sources and are applicable to fossil-fired combustion sources (1). Continuous monitors for opacity (transmissometers) are required to be installed on these sources to verify the maintenance and satisfactory operation of control systems used to meet the emission standards (2). Reference Method 9 is the observer method of measuring the opacity of the plume which forms as the particulate matter exits the stack (1). The Lidar (light detection and ranging) technique is an electro-optical instrumental technique to remotely measure the opacity of the plume (3)(4). The transmissometers are installed in the stack or in ducts leading to the stack and measure the opacity of the gas stream in the stack or duct prior to its exiting the stack.

The Stationary Source Emissions Research Branch (SSERB) of the Environmental Sciences Research Laboratory has had in its program during the past three years tasks to generate a data base of concurrent measurements of in-stack gas opacity (O_s) and plume opacity (O_p) for emissions from various industries. The purpose of these measurements was to identify those industries wherein the plume and in-stack opacities do not agree. Measurements conducted to date on combustion sources burning coal with sulfur $\leq$ 2% show that O_s and O_p are comparable (5)(6). These results would imply that no significant (observable effect on opacity) physical or chemical transformation was occurring in the contents of the gas stream as it was transported through the stack.

Similar opacity measurements were made on a power plant burning oil with 2.4% S (sulfur) and 200 ppm to 600 ppm V (vanadium). In contrast with opacity measurements made at sources burning coal or oil of lower sulfur content, the plume opacity was found to be significantly higher than the in-stack opacity. At this oil-fired power plant a concurrent study was being conducted on sulfuric acid emissions. The results of this acid study support the conclusion that a physical transformation occurs as the gas stream exits the stack and enters the atmosphere. The following phenomenon is indicated: The sulfuric acid is above its dewpoint at stack temperatures in excess of 150°C and does not affect the in-stack opacity. When the gaseous sulfuric acid leaves the stack and is cooled to ambient air temperatures which are below its dewpoint, it condenses and the sulfuric acid droplets increase the plume opacity. Additional studies have been conducted and are ongoing to obtain more data and understanding of the effect of sulfuric acid emissions on plume opacity for various operating conditions, fuel composition, and control systems for a number of fossil-fuel-fired utilities. This paper presents and discusses the results of the above work that SSERB has conducted thus far.

The sulfur oxides potentially present in the stack gas stream at temperatures above the sulfuric acid dewpoint are as shown in Figure 1. The free H_2SO_4 and SO_2 are not sensed in the measurements of the opacity of the stack gas stream. In the plume with the temperature of the gas stream dropping below the acid dewpoint and approaching ambient air temperature, the free H_2SO_4 condenses to form acid droplets. The condensed acid droplets and the acid adsorbed on the fly ash add to the opacity of the plume. In our studies, O_s was measured by transmissometers, and O_p was measured by human observers or by a Lidar system; in some instances, O_p measurements were made by both of these methods.

COMBUSTION SOURCE FEATURES

Plume opacity measurements were conducted in conjunction with emissions characterization studies at two oil-fired and three coal-fired power plants. Table 1 summarizes the physical and operating features of the plants.

There is a marked difference in composition of the fuel utilized in the oil-fired sources in contrast to the coal-fired sources. The ash content of oil was two orders of magnitude less than the ash content of coal and the sulfur content of the coal was from two to four times the sulfur content of the oil. In addition, very high vanadium concentration (590 ppm) was found in the Venezuelan oil. Excess boiler oxygen was typically in the 3% to 5% range except for Plant A which operated at very low oxygen levels at about 0.2%. Oil-fired sources had no emission controls; however, fuel additives were used to minimize corrosion problems and did provide some reduction in sulfate emissions (7). Coal-fired sources had either particulate emission controls (electrostatic precipitators, ESP) or both particulate and gaseous emissions controls (2 stage wet scrubbers).

SAMPLING LOCATIONS

Sampling locations for all in-stack measurements were at a common location between the emission controls and the stack except for Plants M and LC. At Plant M all in-stack measurements were at a common location in the stack proper. At Plant LC in-stack opacities were monitored in breechings leading into the stack, and all other in-stack measurements were at the output of one of eight scrubber modules that operated in parallel for the total boiler output of 820 MW. Each module in effect handled about 100 MW of power output. Except as noted, plume opacities were measured within one stack diameter of the stack exit.

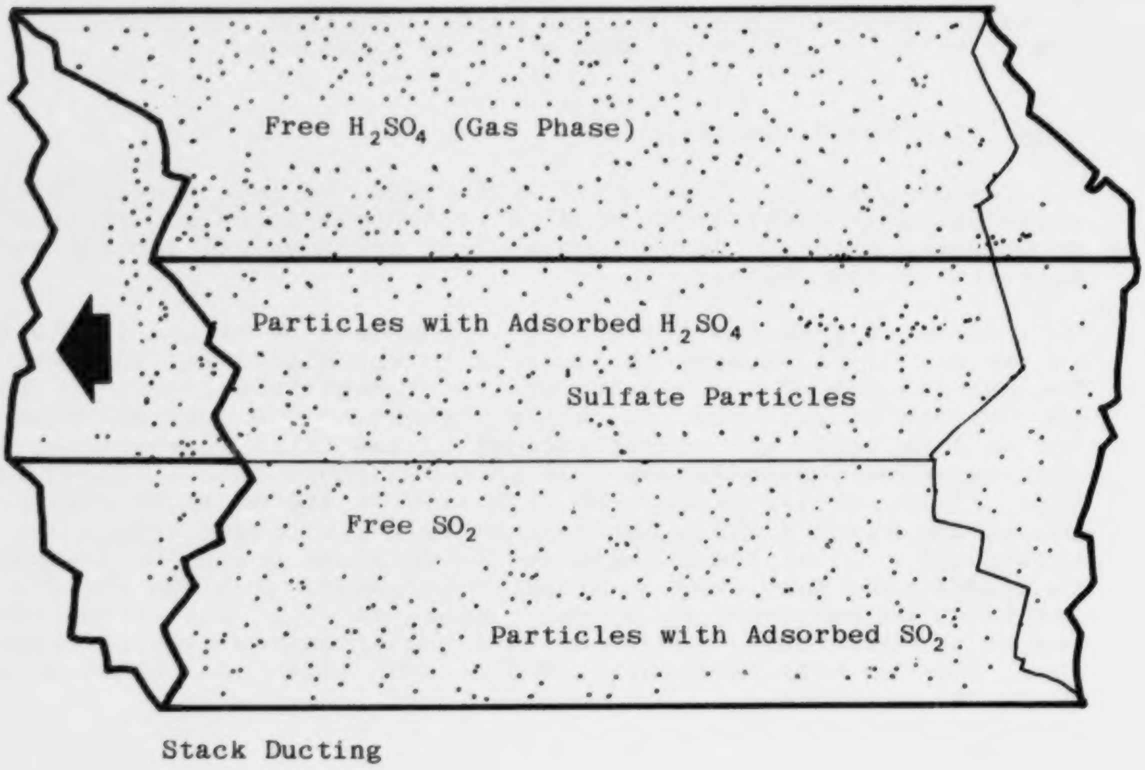
Free H_2SO_4 (Gas Phase)
Particles with Adsorbed H_2SO_4
Sulfate Particles
Free SO_2
Particles with Adsorbed SO_2
Stack Ducting

Figure 1. Sulfur oxides present in the stack gas stream.

Table 1. Summary of Physical and Normal Operating Features of Power Plants Studied

Plant	Fuel Burned	Stack			Fuel Content			Excess[a] Boiler O_2(%)	Emission Controls	Power Output (MW)
		Height (m)	Diameter (m)	Tempera- ture (°C)	Ash (%)	S (%)	V (ppm)			
A	Oil	150	6.8	160	0.17	2.4	590	0.2	only fuel additives	525
M	Oil	60	3.0	127	0.07	1.2	15	3.0	only fuel additives	190
P	Coal	88	4.1	154	8.0	3.3	99	5.0	ESP	100
MC	Coal	178	4.7	166	14.0	3.9	35	4.0	ESP	330
LC	Coal	213	7.0	77	30.0	5.4	50	3.8	2-stage wet scrubber (particulate plus FGD)	820

[a] As measured at economizer outlet.

RESULTS

Emission data were obtained on particulate concentration, SO_2, and sulfates under various operating conditions of the boiler (excess O_2) and of the control systems (cutting back on electric fields of ESP). Opacity data, however, were obtained concurrently for a limited number of operating conditions. The Lidar system was inoperative and undergoing repairs during the studies on the coal-fired sources. Plume opacity data in these instances were limited to Method 9. Poor weather conditions (fog) also restricted plume observations during the study at Plant LC.

Data from the various plant studies on emission concentrations of gross particulate matter, SO_2, total water soluble sulfates ($SO_4^=$), plume opacity, and in-stack opacity were reviewed. As much as possible, data were selected for those periods of time when these measurements were made concurrently. Tables 2, 3, and 4 are a consolidation of these data. Table 2 summarizes the emission data for oil-fired power plants without any emission control systems, Table 3, for coal-fired power plants with ESP controls, and Table 4, for a coal-fired power plant with 2 stage wet scrubbers (particulate control plus flue gas desulfurization, FGD). Various constraints, such as number of available sampling ports in a given location, did not permit the desired measurements to be executed concurrently at Plant LC, and this is reflected in the data in Table 4. These data represent sampling visits to this source on three different dates.

Figure 2 graphically portrays the data of Table 2 showing the comparison of the plume opacity data with the in-stack opacity data at the oil-fired power plants. Figure 2 also provides data on the effect of additional condensation on plume opacity with cooling of the plume downstream of the stack exit location.

DISCUSSION

At the oil-fired power plants M and A (Table 2), the most distinguishing features are the vanadium content of the fuel oil, levels of excess O_2, and their impact on plume opacity. Plant M was burning domestic fuel oil with about 15 ppm V and 1.2% S compared to Plant A which was burning Venezuelan fuel oil with 590 ppm V and 2.4% S. Both plants utilized fuel additives. A significant difference between plume and stack opacity existed for both fuels and for different levels of excess O_2.

The plume opacity at Plant A at normal operation was 31% at the stack exit and above the opacity emission standard of 20%.

Table 2. Emission Characterization Data for Oil-Fired Power Plants Without ESP

Date	Time	Part. (mg/Nm^3)	SO_2 (mg/m^3)	$SO_4^=$ (mg/m^3)	$SO_4^=/SO_x$ (%)	Plume Opac. (%) Lidar	Plume Opac. (%) Obs.	In-Stack[a] Opac. (%)	Remarks
Plant M									
8/10/76	1115-1215	27	1,600	68	4.1	10±2	6±1	2-3	15 ppm V; 4% O_2
Plant A									
8/19/76	1125-1145					31±4	30±1	18-22	590 ppm V; 0.2% O_2
8/19/76	1145-1200					45±3[b]	52±2[b]	18-22	590 ppm V; 0.2% O_2
8/17/76	1145-1205	250	3,800	340	8.2	23±3	42±1	11-15	590 ppm V; 0.4% O_2
8/19/76	0945-1000	390				23±2	37±2	11-15	590 ppm V; 0.6% O_2
8/19/76	1000-1015	390				54±3[b]	61±2[b]	11-15	590 ppm V; 0.6% O_2

[a] Transmissometer measurements.

[b] Measurements about 3 stack diameters (15 meters) downstream of stack exit.

Table 3. EPA Multispectrometer XRF Analyzer Element Sensitivities and Detection Limits (2)

Element	Sensitivity, counts/100 sec per μg/cm	Detection limit (100 sec, 3σ) ng/cm^2	Element	Sensitivity, counts/100 sec per μg/cm^2	Detection limit (100 sec, 3σ) ng/cm^2
F	220	149	Co	16540	3
Na	534	29	Ni	14504	10
Mg	10280	2	Cu	18880	43
Al	8074	3	Zn	21066	7
Si	11614	3	As	17125	10
P	13392	15	Se	22922	12
S	28013	9	Br	50340	28
Cl	25394	9	Cd	17303	2
K	121286	2	Sn	14800	2
Ca	87817	2	Sb	31100	4
Ti	85635	2	Ba	25000	7
V	18010	7	Pt	6812	20
Cr	7484	19	Au	8498	91
Mn	17522	14	Hg	5776	90
Fe	13300	18	Pb	16583	30

Table 4. Emissions Characterization Data for Coal-Fired Power Plant LC with FGD[a]

Date	Time	Part.[b] (mg/Nm^3)	SO_2[b] (mg/m^3)	$SO_4^=$[b] (mg/m^3)	$SO_4^=/SO_x$[b] (%)	Plume[c] Opac. (%)	In-Stack[d] Opacity (%)
9/19/77	1014-1121		2,000	190	8.7		
9/19/77	1201-1309		3,100	260	7.7		
9/19/77	1390-1500		4,200	170	3.9		
9/19/77	1528-1635		5,500	170	3.0		
11/2/77	1529-1629	240					59-67
11/3/77	1345-1445					75	62-71
11/3/77	1530-1630	270					62-71
4/3/78	1245-1345	350				>90	>90
4/3/78	1515-1615	320				>90	>90
4/4/78	1145-1245	220				>90	>90
4/4/78	1345-1445	280				>90	>90
4/5/78	0930-1030	260				>90	>90
4/5/78	1130-1230	280				>90	>90

[a] 30% Ash, 5.4% S, 50-ppm V, 820 MW.

[b] Measurements made on one of 8 parallel FGD modules.

[c] Observer measurements.

[d] Transmissometer measurements at stack breeching.

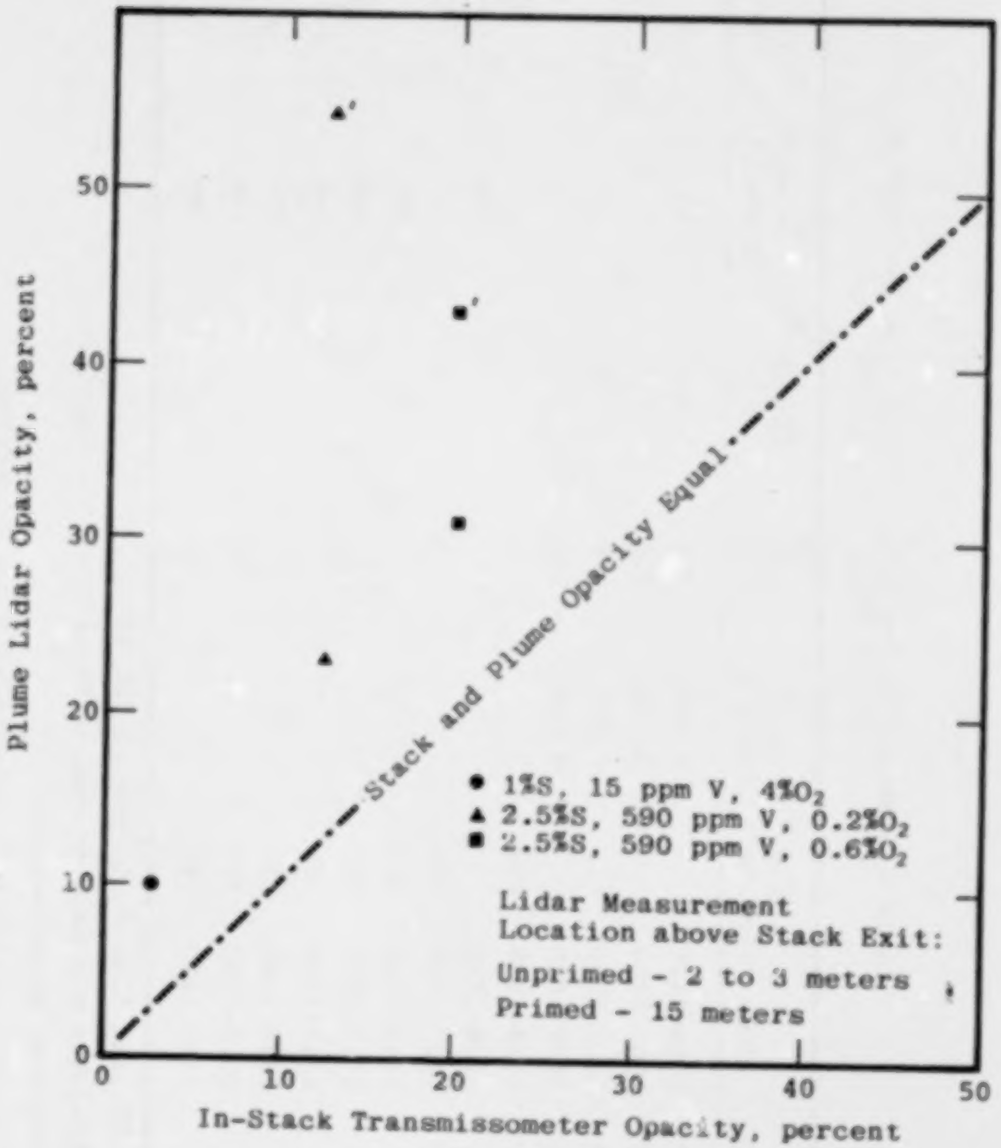

Figure 2. Concurrent plume and in-stack opacity data for emissions from oil-fired power plants.

The opacity increased markedly to 43% further downstream as more condensation of sulfuric acid occurred with cooling of the plume. The observers tended to read higher opacity values than the Lidar.

Both solid particulate matter and condensed sulfuric acid (liquid droplets) affect opacity. Unfortunately, concurrent data are not complete in Table 2, but qualitative data from acid emission measurements in other studies (8)(9)(10) reinforce some observations which can be made from Table 2. The concentration of solid particulate matter increased as excess O_2 for combustion was decreased to reduce acid formation. We attribute this to unburned carbon soot particles which have been observed in a related study (11). The increase of in-stack opacity with decrease in excess O_2 demonstrates this. Since the acid is in the gas phase in the stack, a decrease in acid with a decrease in excess O_2 does not affect the in-stack opacity data or the above interpretation of the data. As a matter of fact, the possibility of reduced sulfate salts exists with the decreased acid, and this would tend to counteract the effect of the unburned carbon and imply a greater impact of acid on stack opacity than was actually observed.

In the plume, the acid (at temperatures below its dewpoint) appears as liquid droplets after condensation. With increased excess O_2, the increased acid and sulfate salts tend to increase the plume opacity, but a counteracting effect is the concurrent reduction in unburned carbon resulting from more complete combustion of the oil. Since the condensation of the acid is a function of the plume temperature, one can infer on a semi-quantitative basis the contribution of the condensed acid in the plume opacity relative to that of the solid particulate (both unburned carbon and sulfate salts) by a comparison of the plume opacity at the exit to that downstream of the exit. At 0.2% O_2, the plume opacity increase was from 31% to 43%. At 0.6% O_2, the increase was from 23% to 54%, indicating the presence of more acid at higher excess O_2 levels. The impact of the acid may actually be more than indicated because dilution of the plume downstream can reduce the opacity and counteract the effect of the increase in condensed acid.

It is of interest to note that there appears to be an increase (56%) in particulate loading as determined by Method 5 with an increase in excess O_2 (Table 2, Plant A). One might expect a decrease because of a reduction in unburned carbon with more complete combustion. There is the possibility of an increase in measured particulate loading due to the collection of the gaseous acid and sulfate salts by Method 5. Related studies in our laboratory have shown the glass fiber filter to be a good collector of the gaseous acid (12). One can postulate that two overlapping functions (one an increase in sulfate salts and acid, and another a decrease in unburned carbon with increasing excess O_2) contribute to the particulate loading. The former will be a curve with a positive slope, the latter a curve with a negative slope. The resulting curve on particulate loading as a function of excess O_2 would have a positive or negative slope depending upon which function has the steeper slope. The resulting curve would approach a straight line (zero slope), as the two functions tend to exactly counteract each other. Consequently, depending upon the amount of excess O_2, the particulate loading may be on either the rising or declining slope of the curve, or it may be more or less constant.

The emission characterization data for high sulfur (>2% S) coal-fired power plants with ESP controls show no significant difference between plume and in-stack opacity under normal ESP operation or with reduced electric fields in the ESP's. It is possible that the high ash content of the coal and resulting high particulate loading in the emission have a predominant effect on the in-stack and plume opacity. In-stack opacity at normal operation of the ESP was close to the opacity emission standard for new sources and higher than that for the oil-fired power plants. The ratio of $SO_4^=$ to particulate matter for the coal-fired emissions is <1 and for the oil-fired emissions, >1.

The stack gas environment for the coal-fired power plant (LC) with particulate and gas controls (2 stage wet scrubber) was unlike that for plants with ESP controls. The stack gas temperatures were below the sulfuric acid dewpoint, and the water vapor content from the wet scrubbers was high. The result was that sulfuric acid will appear in the gas stream as condensed acid droplets, and these directly affect the in-stack opacity.

Concurrent emission data could not be obtained for Plant LC (Table 4) in the same manner that it was for Plants P and MC (Table 3) because the required number of sampling ports was not available. Nonetheless, the data obtained from the three visits to Plant LC do permit some qualitative observations. The emission data on the particulate loading appear to fall within a narrow range of values indicating consistent plant operation. The plume and in-stack opacity data show no significant difference, but the very high opacity values are not consistent with the particulate loading, size, and composition normally associated with fly ash emissions. Optical transmittance measurements conducted at different wavelengths during the study gave data that varied with wavelength in the visible portion of the spectrum (13). This variation with wavelengths is indicative of submicron size distribution. The submicron size was also substantiated with in-stack impactor measurements (14). The acid composition of the gas stream was substantiated by the controlled condensation measurement data (7). In this case, we attribute the high in-stack opacity levels to fine particle concentration with a mass mean diameter in the submicron size range and with a significant percentage of the composition consisting of condensed sulfuric acid.

There are a number of important questions raised by the data obtained thus far. More studies are needed to adequately address these questions and to determine the variation of these pollutant emissions with operating parameters. The questions can be briefly stated as follows:

- What is the quantitative distribution of H_2SO_4 in the gas stream between free acid and acid adsorbed on particulate matter?
- What is the distribution of the sulfate ion ($SO_4^=$) between acid and salts?
- What is the size distribution of acid and salts?

There is need for more data on the physical properties of H_2SO_4 in both the stack and plume environments to support proper interpretation of optical data.

SUMMARY

Emissions from oil-fired power plants without emission controls and coal-fired power plants with ESP's and with FGD systems were characterized for plume and in-stack opacity, SO_2, $SO_4^=$, and mass concentration. Sulfuric acid content of the emissions from the oil-fired power plant had a significant effect on the plume opacity but no effect on the in-stack opacity. In the case of the coal-fired power plants with ESP's, the in-stack and plume opacities were essentially the same. This led to the conclusion that the concentration of acid was low relative to the non-acid particulate such that the acid did not contribute to any significant degree to the opacity of the plume beyond that normally associated with the fly ash. The in-stack and plume opacities of the emissions for the high sulfur coal-fired power plant with the 2 stage wet scrubber system were comparable but significantly high (70% to 90%). The high opacity was attributed mainly to the sulfuric acid content of the emissions and to submicron size of the particulate matter.

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Query: Is There a Connection between the Expansion of Areas of Acid Rain and a Shift from Coal to Oil for Small-Scale Heat Needs?

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ABSTRACT

Odén's classic maps show the "explosion" of acid rain over Northwest Europe between 1956 and 1966. Is there a connection between Odén's data and the shift from coal to oil for much of Europe's small-scale heat needs?

Since the oil in question had a much higher sulfur content than the coal it replaced, emissions of sulfur dioxide sharply increased. Historic combustion data suggest that a small oil furnace may emit appreciably more sulfuric acid mist than a small coal furnace, even when the fuel that is used contains low levels of sulfur.

Before the query can be answered, we need data on emissions of sulfuric acid mist from real-world oil furnaces, even those firing low-sulfur oil, as well as data on atmospheric conversion of sulfur dioxide. The acid emissions data should be for furnaces representing a wide spectrum of age, type, history, condition of maintenance, firing practice, etc. Needed data on emissions from small coal furnaces of modern design will be acquired at VPI & SU in a Coal Combustion Workshop emphasizing state-of-the-art furnaces up to about 3 megawatts (thermal).

In the late spring, we will commission our first furnace (an English fluidized-bed unit at 0.3 megawatt) and measure emissions of trace elements.

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Odén's classic maps of acid rain over Northwest Europe between 1956 and 1966 show the "explosion" of this phenomenon in those years (1).

Those were the years, however, when Western Europe shifted from coal to oil as its "growth fuel." It is evident from Table 1 that most planners chose oil for new sources of heat. (In Table 1, Western Europe includes Greece and Yugoslavia.) Since coal for steel and large-scale electricity generation continued to increase, some replacement of coal by oil for heat needs on a smaller scale must have occurred.

Table 1. Annual Consumption of Coal and Oil in Western Europe, Expressed in Millions of Metric Tons of Hard Coal Equivalent

Year	Coal	Oil
1950	464	86
1958	540	189
1966	486	516

Ockham's razor ("Pluralites non est ponenda sine necessitate" = Multiplicity ought not be posited without necessity) is a useful principle for the engineer, who must often blend engineering science of limited applicability with imperfectly understood art in order to make his design and to accomplish his job. Perhaps, then, an engineer will be forgiven if he associates the spread of acid rain in Western Europe with the shift to oil.

Further, it may be reasonable to consider the simplest explanation of this association. Combustion engineers have long recognized that oil furnaces tend to emit a good deal more sulfuric acid mist, other factors being equal, than do coal furnaces. Krause (2) reviewed the evidence prior to 1959.

We might, parenthetically, remember that in the 1960's engineers developed the practice of limiting the excess air to large utility boilers fired with oil, and this practice came into use only late in that decade. It would no longer be true to say that oil furnaces inherently make more sulfur trioxide than coal furnaces, since a carefully managed oil furnace can make less. Combustion with low excess air, however, is a practice limited to relatively large boilers and is not accessible to the operator of a small furnace.

The simplest explanation of Odén's maps, then, is that the growth of oil combustion produced a large increase in primary emissions of sulfuric acid mist. Is this the correct explanation? It would be foolhardy to do more than put it forward gingerly as a hypothesis well worth examining.

What is missing, however, for a thorough test of the hypothesis is an adequate data base on emissions of sulfuric acid mist from oil furnaces, especially from those of smaller size. Few measurements appear to have been made, for example, on furnaces in the roughly 300 kilowatt to 6 megawatt thermal range of size (30 to 600 boiler horsepower; 1 to 20 million Btu's per hour), which accounts, for example, for roughly one-half of the emissions of sulfur oxides in New York City. No measurements have been made, as far as the author is aware, that are representative of actual firing practices over typical daily and annual operating cycles of such equipment.

Another curiosity, which the razor suggests might reasonably be set alongside Odén's maps in our minds, is the persistence of high levels of sulfate particulate matter in New York City after emissions of sulfur dioxide have sharply declined. Seeking a simple explanation, related to our hypothesis concerning acid rain, we might consider the long-appreciated fact that emissions of sulfuric acid mist from oil firing do not track the sulfur level of the oil. Krause (2) reviewed the evidence. Unpublished data taken by KVB, Inc. on five small furnaces (between 84 and 430 boiler horsepower) burning low-sulfur oil (between 0.09% and 0.28% sulfur) tend to confirm the historic evidence that conversions of fuel sulfur to the trioxide in this low range can run many times greater than the roughly 1% conversion to be expected for oil at 2.5% sulfur.

A subjective observation by a former resident of New York City would be that something like one oil furnace out of twenty is managed by an operator who daily puts out dense clouds of black, sooty smoke for several fifteen-minute intervals, in summer as well as winter. No doubt it will be difficult to develop a good figure for input of sulfuric acid and sulfate particulate matter into New York City's air, but the effort should include measurements for poorly-run equipment. Obviously, measurements would need also to be made for furnaces representing a wide spectrum of age, type, history, and conditions of maintenance.

Returning to Odén's maps, we should remember that the oils burned in Western Europe in the 1950's and 1960's tended to have higher sulfur levels than European coals, and so the data of Table 1 imply a large increase in emissions of sulfur dioxide. Perhaps, as well as the increase in primary emissions of sulfuric acid, there also may have been a significant increase in the synthesis of acid from sulfur dioxide in the atmosphere.

Granted this probability, we may still regard it as curious that acid rain did not draw attention before the sharp expansion of oil firing. We may, therefore, still seek parsimonious hypotheses to test. There is a body of thought that associates conversion of sulfur dioxide to trioxide in the atmosphere with presence of particulate matter. Perhaps a part of the explanation of Odén's maps is associated with earlier deposition of sulfur trioxide adsorbed upon larger particles from the stack of a coal-fired furnace (even one fitted with a good precipitator). Perhaps oil combustion is placing ultra-fine particulate matter into the atmosphere, laden with adsorbed sulfate, that travels long distances.

These suppositions would fit the recent evidence that sulfate particulate matter in New York City tracks the level of such matter at a rural sampling station upwind of the city (3).

There is also a body of thought that associates the persistence of high levels of sulfates in urban atmospheres with conversion of sulfur dioxide, even at the new low levels, upon particulate matter found in these atmospheres. Some light on this opinion might be shed by study of selected cities that represent extremes in the weight ratio of smoke to sulfur dioxide. This ratio is low, for example, in London (about 0.2) and is astonishingly high in Madrid (1.3 to 1.5) (4).

Perhaps Ockham's razor is a poor guide in this complex situation. It does, however, point to a serious gap in our information concerning emissions of sulfuric acid mist from combustion, viz., from small oil furnaces.

Lest we be in for yet more surprises, we need better data for emissions of all kinds from the variety of new coal furnaces that may find increasing favor in the years ahead.

Virginia Polytechnic Institute & State University is setting up a Coal Combustion Workshop that will emphasize state-of-the-art furnaces up to about 3 megawatts thermal. We hope to commission our first furnace, an English fluidized-bed unit at 0.3 megawatt, within the next few months. Our primary emphasis will be upon extension instruction of the general public, but we will routinely study emissions from the dozen or so furnaces we hope to acquire.

Let no one suppose that the hypotheses set forth here concerning Odén's maps imply a defense of Europe's historic practices for burning coal. The author himself experienced two of London's killing smogs, in late 1958 and late 1959. Therefore, he was much impressed with the dramatic changes realized during the 1960's from the implementation of Britain's Clean Air Act of 1956. Few Americans, however, appreciate, as the English do, that small coal furnaces can be clean. As a Nation, we remember the dirt and labor of most small coal fires of the past. We remember the smoke and soot of cities like St. Louis and Pittsburgh. The primary aim of VPI & SU's Coal Combustion Workshop will be to demonstrate that coal can be clean.

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Report of the Working Group on Characterization of Gaseous Sulfur Oxides Emissions

Arthur M. Squires, *Reporter*

This Working Group's objective was to review the status of characterization data for gaseous sulfur oxides emissions. Its conclusions and recommendations are as follows.

STATUS AND VALIDITY OF AVAILABLE DATA

Available sulfur dioxide data are generally reliable and useful for judging sulfur dioxide emissions from combustion sources. The Group noted, however, that measurements of sulfur dioxide need to be accompanied by simultaneous measurements of oxygen level and temperature at the point of measurement. When data are to be used for emission comparisons, not only should the original data be reported, but a sulfur dioxide level that is corrected to a stated standard oxygen level should also be noted. (The level of 3% oxygen has become standard for reporting nitrogen oxide emissions.)

Sulfur dioxide emission rate data are calculated from sulfur dioxide and oxygen concentration measurements and an F-Factor. Emission rate data can also be determined from measurements of flue gas velocity and sulfur dioxide concentration.

The concentration of sulfuric acid vapor from an oil-fired plant reflects a higher conversion of fuel sulfur, given prevalent current firing practices, than the concentration of sulfuric acid vapor from a coal-fired plant. Oil-fired sources tend to produce particulates with high content of soluble sulfate matter. The fraction of soluble particulate sulfates versus acid in coal-fired emissions depends upon the amount and nature of the ash in the coal and may vary widely.

RECOMMENDATIONS

Sulfuric acid emissions data should be reported in parts per million of H_2SO_4 by volume. If the data are reported as mg/Nm^3, or in other units, the conversion factor to ppm by volume should be stated along with the data.

Water soluble sulfate particulates should be reported in mass units of sulfate ion per gas volume (e.g., mg/Nm^3).

Certain additional measurements need to be made in support of sulfuric acid emissions data.

- Furnace oxygen level. This is difficult to measure directly, and no good or convenient sampling technique is available. The Working Group recognized development of a sampling technique as a need for research.
- Temperature and oxygen level at the measuring point.
- Temperature of gases entering the convective pass of a utility boiler, or temperature data generally indicating the time-temperature history of the combustion gases.

In spite of some questions about measurement techniques and conditions of measurement, the available sulfuric acid and soluble sulfate particulate data do make a fairly consistent but incomplete picture. More data are needed to support the picture available today for large utility boilers firing oils of moderate to high sulfur levels. Almost totally lacking are emissions data for furnaces of all types burning low-sulfur oils, e.g., at 0.5% sulfur and below, and emissions data for oil-fired industrial boilers and other smaller furnaces, such as heating units for apartment buildings, business establishments, and the like, most of which now burn low-sulfur oils.

Smaller boilers burning low-sulfur fuels may in combination constitute significant emission sources of sulfuric acid and soluble sulfate particulate matter for important air sheds, and their study is needed. It costs as much to study a small unit as a large one, and budgets will have to reflect this fact.

Workers who conduct studies of conversion of sulfur dioxide in the atmosphere to secondary sulfate particulates (e.g., plume studies) should be aware of the need to have good inputs of emissions data for sulfuric acid and soluble sulfate particulates from the relevant sources. For example, there is need during a plume study to check and record the operating conditions of the plant generating the plume.

For studies of plume opacity, there is need to acquire data on the relative contribution of fly ash and acid aerosol to the opacity of a plume, both in terms of in-stack measurements and of data gathered in the open plume. There is need for data to allow better understanding of the optical properties of plumes:

- Distribution of sulfate ion between acid and particulates.
- Size distribution of mist particles and of other particulates.
- Role of solid particles as condensation nuclei for acid.

Section 2

Particulate Emissions

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Characterization of Fly Ash from Coal Combustion

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ABSTRACT

Fly ash derived from coal combustion contains predominantly spherical particles which consist of an insoluble aluminosilicate glass containing several mineral impurities. An outer layer, 50 to 300 Å thick, is rich in many potentially toxic trace elements in the form of simple and complex sulfates. This layer, which is soluble in water, contains essentially all of the particulate sulfur present in fly ash in the form of sulfate. The actual mechanism(s) of formation of particulate sulfate salts are ill-defined but probably involve adsorption of condensation of gaseous sulfur species onto fly ash surfaces within the power plant stack system.

INTRODUCTION

At the present time approximately 80% of the electric power generated in the United States is derived from the combustion of fossil fuels. Of this total, coal combustion accounts for approximately 70% with the balance made up by natural gas and oil. Furthermore, it is now clear that increased coal utilization will be the primary means of meeting the nation's electrical energy needs for the next several decades at least.

It is well established (1) that sulfur present in coal is mobilized, almost quantitatively, into the stack gas stream as a result of combustion in coal-fired power plants. In conventional combustion operations, most of this sulfur is present as sulfur dioxide,

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together with small amounts in the form of sulfur trioxide, sulfuric acid, and particulate sulfate salts. The latter are associated primarily with fly ash particles whose physical and chemical characteristics may play a controlling role in determining the environmental impact of both emitted sulfate salts and of other sulfur species (e.g., sulfur dioxide) which may interact with fly ash following emission.

It is the purpose of this paper to summarize the available information about the physical and chemical characteristics of coal fly ash and to assess the status of present knowledge about sulfur species associated with fly ash. In both cases emphasis is placed on what is known about the fundamental processes which control the formation, transformation, and subsequent environmental behavior of coal fly ash and its sulfur-containing constituents.

NATURE OF COAL FLY ASH

A number of workers have undertaken detailed physical and chemical studies of coal fly ash (2-5), and its general characteristics are now quite well known. It is, however, important to note that fly ash derived from different power plants may exhibit considerable variability due, primarily, to differences between coal types and the nature of the combustion conditions. In this regard, combustion temperature is a very important factor insofar as it determines whether or not the fly ash matrix is molten at any stage and whether potentially volatile species actually experience a vapor phase history. It is also extremely important to recognize that most studies of fly ash are conducted on samples which are retained by particle control devices so do not truly represent material emitted to the atmosphere.

Morphology and Matrix Composition

Derived from mineral impurities present in the coal, coal fly ash particles are primarily inorganic in nature. Consequently, the amount of mineral matter present in a given coal strongly influences the particle emission factor for that coal. The major elemental constituents of coal fly ash are Si, Al and Fe, together with minor amounts of Ca, Mg, K, Na, Ti, and S. Some typical concentration ranges of these elements in U.S. coal fly ashes are presented in Table 1 (6). In general, fly ashes derived from western U.S. coals have a higher ash content and exhibit higher alkali and alkaline earth metal contents than do those from eastern coals, which are typically higher in sulfur.

Table 1. Typical Matrix Element Composition Ranges of Some U.S. Coal Fly Ashes Expressed as Weight Percentages of the Oxides

	Matrix element composition, wt-% of oxide
Major constituent	
Al_2O_3	14-30
SiO_2	22-60
Fe_2O_3	3-21
K_2O	0.2-3.5
CaO	0.5-31.0
Minor constituents	
Li_2O	0.01-0.07
Na_2O	0.2-2.3
MgO	0.7-12.7
TiO_2	0.6-2.6
P_2O_5	0.1-1.1
SO_4 *	0.1-2.2

*Soluble sulfate

During combustion in a modern coal-fired power plant, the mineral impurities in coal melt and form small, mostly spherical, particles. The extent to which these molten particles coalesce or disintegrate into even smaller droplets is determined in part by the geometry, flow characteristics, and combustion conditions within the plant. Consequently, the size distribution of the particles produced may vary significantly between different plants. In a few plants of obsolete design (e.g., chain grate stoked), as well as in modern fluidized bed plants, combustion temperatures are not sufficiently high to melt the fly ash matrix, so that irregularly shaped particles are formed. Since these cannot readily disintegrate, their size distribution is generally centered around larger, median values than those encountered with spherical fly ash particles.

The aerodynamic equivalent mass median diameters of coal fly ashes in the absence of particle control devices typically lie in the range 8 μm to 30 μm (7), and the mass is reasonably approximated by a log-normal distribution. The mass median diameters of fly ashes emitted from control devices are considerably smaller than indicated above and depend largely on the collection efficiency of the control devices. In the case of electrostatic precipitators, mass removal efficiencies in excess of 98% are often achieved, and aerodynamic mass median diameters of emitted fly ash are typically in the range 0.5 μm to 2 μm.

While a number of distinct morphological forms of fly ash can be distinguished (10), only three are highly abundant. The first involves solid, or slightly voided, spheres and accounts for most fly ash particles having physical diameters less than about 5 μm. The second morphological form consists of hollow spheres whose interior voids are filled with carbon dioxide at a pressure of about 0.2 atm (4). These particles predominate in the physical diameter range 10 μm to 60 μm. Finally, and most intriguing, are hollow particles filled with large numbers (10 to 200) of small solid particles. This encapsulation phenomenon is encountered primarily for particles in the physical diameter range 20 μm to 60 μm (8). The phenomenon of particle encapsulation in fly ash is not fully understood; however, there is good evidence to show that encapsulated particles are actually formed inside their hosts so are not available to interact with external vapors and gases such as SO_2 (9).

As a result of the widespread occurrence of hollow and encapsulating fly ash particles, the measured density of coal fly ash is essentially unrelated to the density of the matrix material. X-ray and electron diffraction studies of fly ash indicate that the matrix consists, for the most part, of an aluminosilicate glass together with small amounts of the minerals α quartz (SiO_2), mullite ($3Al_2O_3 . 2SiO_2$), hematite (Fe_2O_3), and magnetite (Fe_3O_4). Fly ashes derived from western U.S. coals also have some crystalline gypsum ($CaSO_4 . 2H_2O$) and lime (CaO). It is apparent, therefore, that coal fly ash is highly heterogeneous in nature and is likely to exhibit low aqueous solubility.

Trace Element Distribution

The specific concentrations (μg/g) of individual trace elements in coal fly ashes depend primarily on the trace element content of the original coal. In general, a fly ash which contains high concentrations of one trace element will also have high concentrations of most others as well. However, the relative elemental concentrations encountered in fly ash may differ markedly from those in the original coal due to the different partitioning characteristics of individual trace elements between bottom ash and fly ash. Table 2 lists some typical specific concentration ranges for a number of trace elements encountered in coal fly ash and compares them with values for oil fly ash.

Table 2. Specific Concentrations of Elements in Coal and Oil Fly Ashes

Element	Coal Fly Ash Specific concentration, µg/g	Oil Fly Ash Specific concentration, µg/g
Al	70,000-140,000	100-5000
As	2-500	30
Au	0.004-0.1	--
B	10-600	--
Ba	500-7000	500-10,000
Be	1-10	--
Br	0.3-20	--
Ca	6000-180,000	10-1000
Cd	0.1-50	--
Ce	100-300	--
Cl	10-500	--
Co	5-100	90
Cr	50-300	66
Cs	1-20	--
Cu	50-650	50-2000
Fe	25,000-300,000	10,000-100,000
Ga	10-250	--
Hf	5-10	--
Hg	0.02-0.4	--
I	0.5-7	--
In	0.1-0.3	--
K	1500-35,000	1000
La	35-100	--
Lu	0.5-2	--
Mg	11,000-60,000	500-5000
Mn	50-500	1-100
Mo	5-40	--
Na	1200-18,000	2000-50,000
Ni	5-100	--
Pb	5-1000	200-2000
Rb	40-300	--
Sb	1-15	5
Sc	10-40	--
Se	1-20	5
Sm	10-20	--
Sn	30-30	--
Sr	50-4000	--
Ta	0.5-1.5	--
Th	15-70	--
Ti	3500-8500	--
Tl	2-30	--
U	5-20	--
V	100-500	100-200,000
W	3-10	--
Yb	3-7	--
Zn	50-5000	200-3500

It is now well established (2)(3)(8) that a number of elements, including As, Cd, Cu, Ga, Mo, Pb, S, Sb, Se, Tl, and Zn, tend to increase in specific concentration with decreasing particle size. This is attributed to a mechanism whereby certain elements, or their compounds, are volatilized during combustion and then condense back onto the surfaces of co-entrained fly ash particles as the temperature falls to the dewpoint of each vapor species. A great deal of evidence has been presented in support of this mechanism (2)(3)(10); however, it is becoming increasingly apparent that several additional factors may also operate. For example, recent work (8) suggests that the physical and chemical behavior of individual elements during combustion can be correlated with their geochemical classification. Thus, the chalcophile, lithophile, and siderophile elements exhibit different partitioning behavior which determines their distribution in coal fly ash. In addition, a distinct influence of individual particle matrix composition and specific surface area is observed.

Undoubtedly the most important consequence of the volatilization-condensation phenomenon exhibited by some trace elements is their pronounced enrichment in the region of individual particle surfaces. An example of such enrichment is presented in Figure 1 in which the concentration dependence of lead on depth below the particle surface is illustrated. The importance of this surface enrichment lies in several factors, viz.

(1) It is the particle surface which comes in direct contact with the external environment so that the highest concentrations of potentially toxic and reactive trace elements are mostly readily accessible. A rough comparison of estimated surface and bulk concentrations of several elements in a coal fly ash is presented for illustration in Table 3.

(2) Material present in the region of surface enrichment is readily soluble in aqueous media (Figure 1), thereby rendering the most environmentally undesirable trace elements mobile and available for interaction with the external environment. In this regard it should be recognized that only about 2%-3% of the total mass of coal fly ash is soluble in water.

(3) Conventional analyses of bulk fly ash grossly underestimate the effective concentrations of most trace elements which are actually available for interaction with the external environment (Table 3).

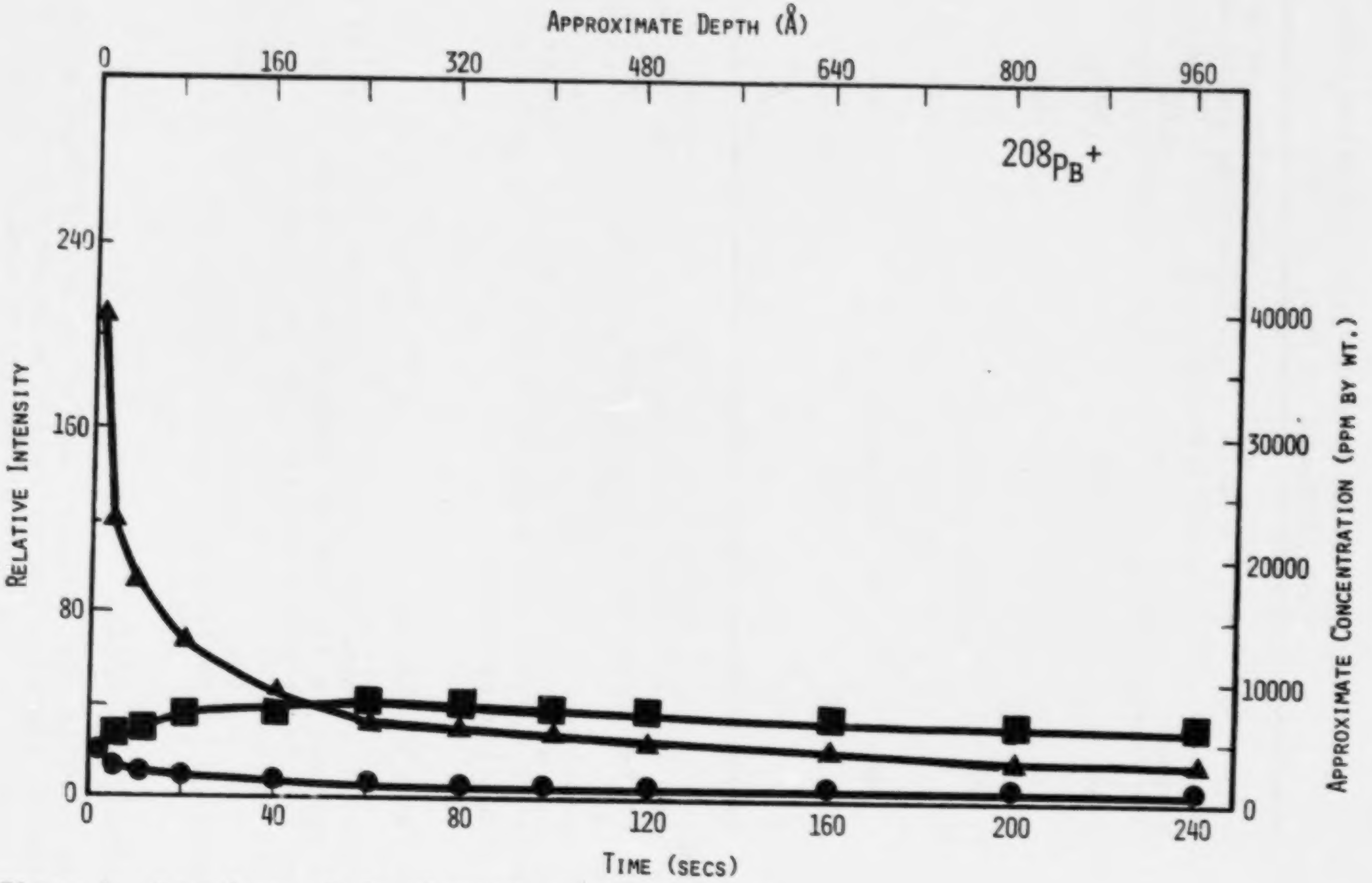

Figure 1. Dependence of the elemental concentration of lead on depth below the surface of a coal fly ash particle before (▲) and after leaching with water (●) and dimethyl sulfoxide (■) as determined by secondary ion mass spectrometry.

Table 3. Estimated Surface Concentrations of Elements in Coal Fly Ash

Element	Bulk concentration, µg/g	Estimated surface concentrated in 300 Å layer, µg/g
As	600	1,500
Cd	24	700
Co	65	440
Cr	400	1,400
Pb	620	2,700
S	7,100	252,000
V	380	760

When one takes account of the fact that condensation of trace metals onto fly ash particle surfaces almost certainly takes place at much higher temperatures than does condensation of SO_3, or adsorption of SO_2, it will be recognized that much of the interaction of sulfur species with fly ash is likely to be with trace metal species rather than with the particle matrix material. This may be extremely important in determining both the nature of the interactions and their resulting products.

SULFUR IN COAL FLY ASH

Current information about the chemical and physical status of sulfur present in fly ash is fragmentary. Nevertheless, a useful picture of its probable behavior can be assembled. For this purpose, it is helpful to consider the inter- and intra-particle distribution of sulfur, its chemical forms, and the probable mechanisms of formation of particulate sulfate salts.

Distribution of Sulfur

As pointed out earlier, sulfur is one of those elements which increase in specific concentration with decreasing particle size (2). However, unlike most of the trace metals, which exhibit such size dependence, a linear correlation between specific concentrations of sulfur and particle surface area is difficult to establish (2)(3). Indeed, separation of the dependences of concentration on physical size, density, and feromagnetism, as illustrated in Table 4, indicates a rather complicated dependence on both particle size and density. The reasons for these dependences are not clear.

Table 4. Distribution of Sulfur Concentration (% by wt) as a Function of Physical Size, Density, and Ferromagnetic Character in Coal Fly Ash

Particle Size (μm)		Density (g/cm^3)			
		<2.1	2.1-2.5	2.5-2.9	>2.9
Nonmagnetic	<20	0.24	0.40	0.22	--
	20-44	0.11	0.48	0.82	0.43
	44-74	0.21	0.37	1.26	1.02
	>74	0.31	0.12	0.48	0.71
Magnetic	<20	--	--	0.16	0.19
	20-44	--	--	0.45	0.09
	44-74	0.10	0.21	0.34	0.28
	>74	--	0.43	0.20	0.14

Analyses of individual particles and groups of particles by means of ion microprobe mass spectrometry and Auger electron spectrometry (10) establishes beyond reasonable doubt that the sulfur associated with coal fly ash is present in a layer of the order of 50 Å thick at the particle surfaces (Figure 2). Furthermore, this layer is sufficiently soluble to enable almost quantitative removal of all sulfur species by continued washing with water or mineral acids. An example of such removal is presented in Figure 3 which illustrates the dependence of sulfate concentration on time in individual washings during Soxhlet extraction of coal fly ash with water at 25°C. (This technique is later referred to as Time Resolved Solvent Leaching, TRSL.)

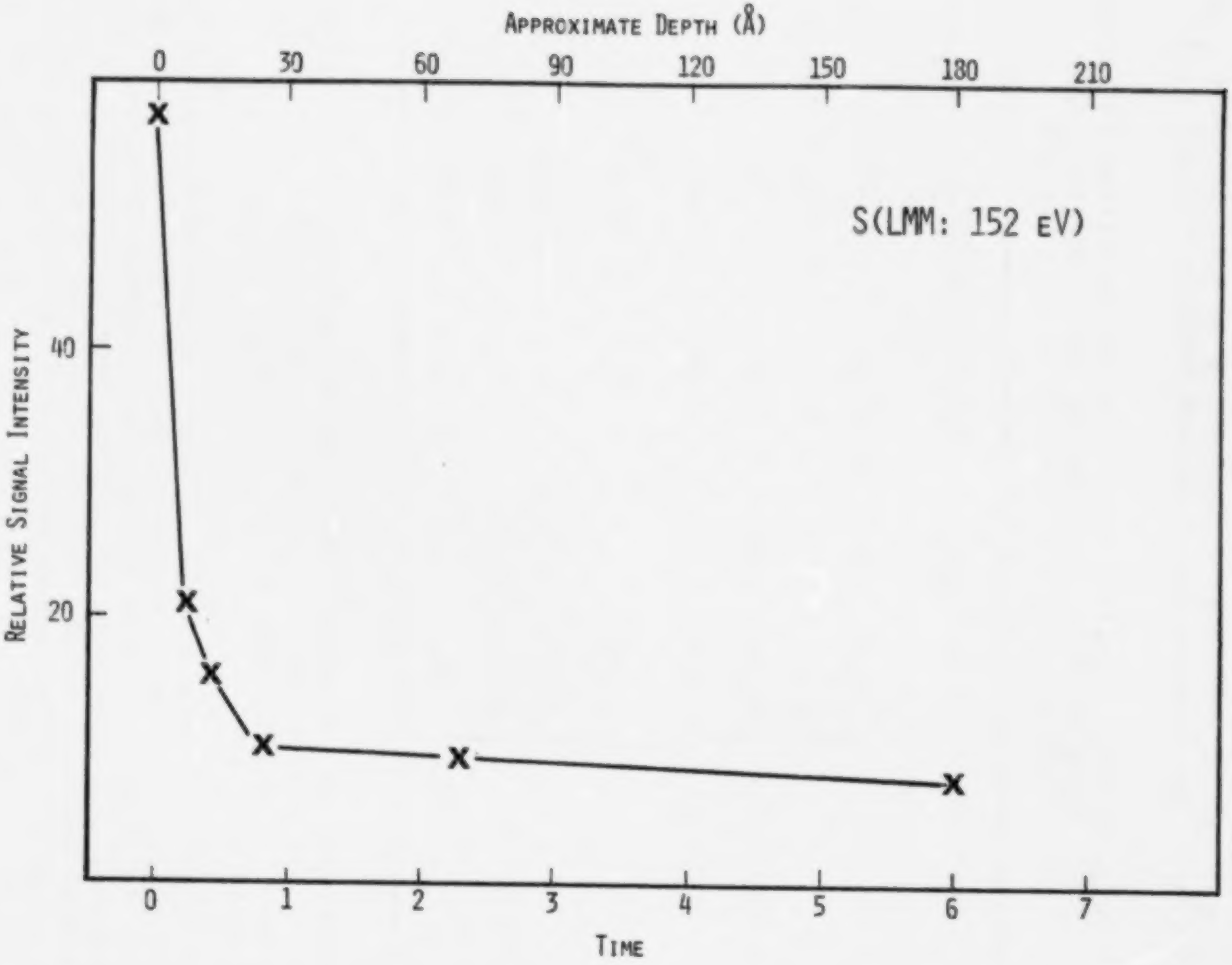

Figure 2. Dependence of the elemental concentration of sulfur on depth below the surface of a coal fly ash particle as determined by Auger electron spectrometry.

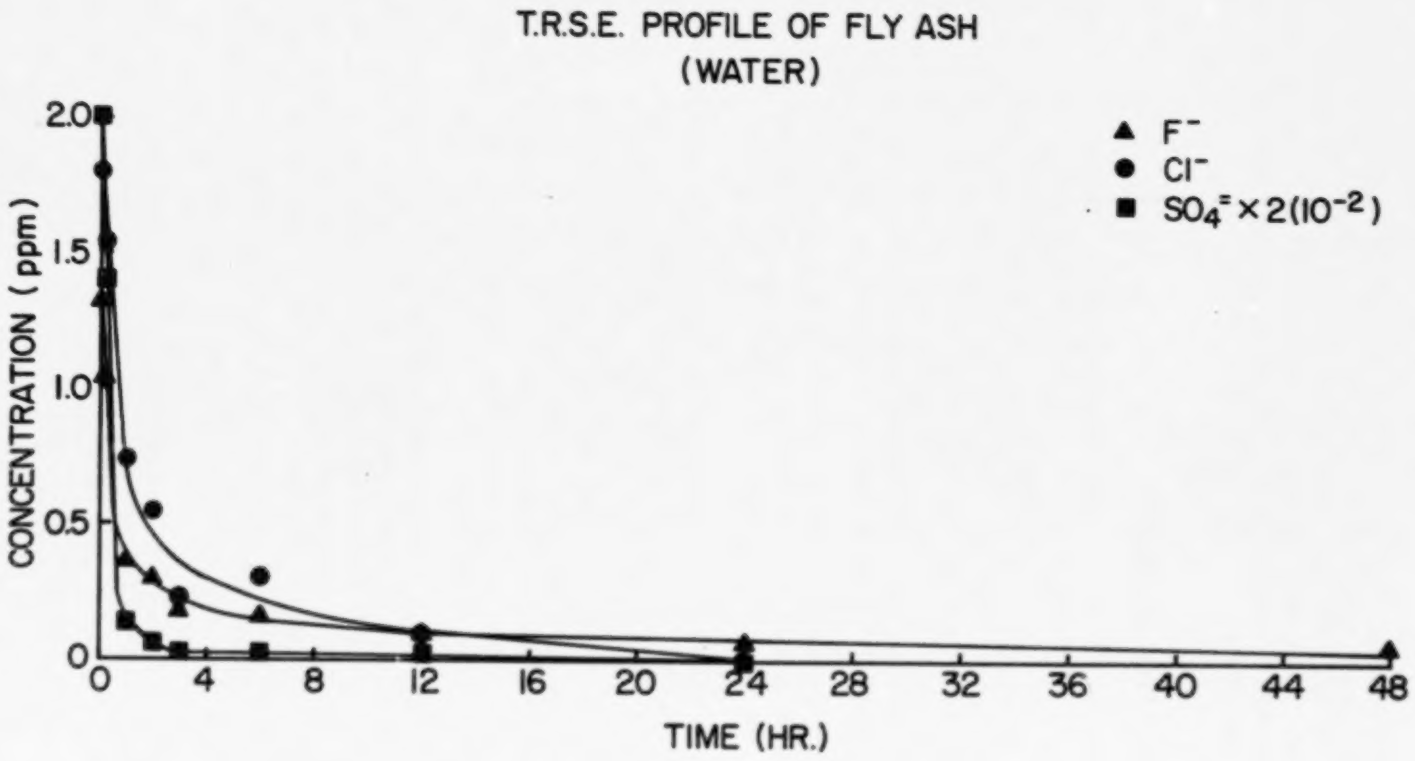

Figure 3. Time resolved leaching profile for sulfate, chloride and fluoride anion extraction from coal fly ash.

Analyses of fly ash which has been exhaustively leached with water indicate that very little, if any, sulfur remains, even though only 2%-5% of the fly ash mass actually dissolves. It is apparent, therefore, that sulfur is, at most, only a trace constituent in the fly ash matrix even though it is a major component of the particle surface layers.

Chemical Forms of Sulfur

Studies of fly ashes derived from the oxidative combustion of coal and oil using Electron Spectrometry for Chemical Analysis (ESCA) show that sulfur is present in the +6 oxidation state (10). Particulates derived from coal conversion processes, which involve reducing conditions, contain sulfur in the -2 oxidation state, however (11). Neither result is unexpected. Time resolved solvent leaching studies of coal fly ash, in which analyses of soluble anions are performed by means of ion chromatography, indicate that sulfate is the only sulfur-containing anion leached by water.

It is probable, therefore, that the sulfur species present in the surface layer of coal fly ash is, at least predominantly, and probably exclusively, in the form of sulfate.

Some evidence is available regarding the cations which are associated with sulfate species in coal fly ash. Thus, X-ray powder diffraction patterns of some fly ashes indicate the presence of either anhydrite ($CaSO_4$) or gypsum ($CaSO_4 2H_2O$). These species are present most commonly in fly ashes derived from western U.S. coals which contain especially high levels of calcium. The two forms result, apparently, from exposure of the highly hygroscopic anhydrite to moisture. In a sense, therefore, the occurrence of gypsum is probably artefactual.

Quite strong indications have also been obtained for the existence of several trace metal sulfates in coal fly ash. Thus, both Fourier Transform Infra Red Spectroscopy and Time Resolved Solvent Leaching (TRSL) provide evidence for the presence of Cd, Co, Cr, Mo, and Ni sulfates in coal fly ash. The alkali metals Ba, Cu, and Ca are also present, at least partly, in the form of sulfates. Even stronger evidence is available (12) for the existence of Al and Fe as sulfates in the surface layer of fly ash.

While definitive evidence is lacking, present indications are that essentially all of the elements present in the so-called surface layer of coal fly ash exist in the form of sulfates. Two points must, however, be recognized. First, the actual sulfate compounds are probably not simple but may consist of mineral forms which may include double salts. For example, the existance of alkali iron tri-sulfates has been suggested (10). Secondly, it is clear (at least in the case of the minor elements such as Ba, Ca, Mg, K, and Na) that a given metal may be present in more than one chemical form. No evidence has been found for the presence of free H_2SO_4 in fly ash particles.

Association of Sulfur with Fly Ash

The fact that sulfur present in coal fly ash is present almost entirely in the so-called particle surface layer provides very strong support for the proposition that sulfur-containing gases or vapors interact with the surfaces of co-entrained fly ash particles in a power plant stack. What is not clear is whether the interaction is via condensation, adsorption, or chemical reaction, or whether sulfur dioxide, sulfur trioxide, or sulfuric acid is the primary reactant.

Simple vapor pressure calculations indicate that condensation of SO_3 and H_2SO_4 is unlikely to occur at the temperatures encountered in a coal-fired power plant. Yet fly ash with well-formed sulfate surface layers is routinely collected at such temperatures (e.g., from electrostatic precipitators). One is inclined, therefore, to rule out condensation processes as being responsible for surface deposition of sulfates unless direct condensation of a metal-sulfate from the vapor phase occurs. As far as we are aware, there is no evidence whatsoever to support such an idea.

By default, therefore, one is left with the process of adsorption of SO_2, SO_3, or H_2SO_4 as being responsible for formation of particulate sulfate salts. In this regard it should be noted that adsorption of SO_2 would require fairly rapid (possibly catalytic) oxidation to the sulfate species.

It is apparent from the foregoing remarks that further research into the mechanism(s) of formation of particulate sulfate salts is required. In this regard, it is stressed that the toxicological implications of particulate sulfate salts make such research far from academic insofar as knowledge of formation mechanisms may well provide information necessary for development of effective control strategies.

CONCLUSIONS

Overall, it appears that the physical and chemical characteristics of coal fly ash are quite well defined. Thus, the material is in the form of spherical particles which consist primarily of an alumino-silicate glass containing several effectively insoluble, mineral forms. On the surface of this insoluble substrate, however, there exists a thin layer (50-300 Å) of readily soluble material which is rich in trace metals and which contains essentially all of the particulate sulfur in the form of metal sulfates.

It seems highly probable that the soluble sulfate layer present on the surface of coal fly ash particles is formed by gas-to-particle conversion of sulfur species involving adsorption and/or condensation processes. Certainly, the necessary increase in specific concentration of sulfur with decreasing particle size is observed, although agreement with theoretically predicted size dependences is poor. Essentially nothing is known about the actual species which are involved in gas-to-particle conversion.

Due to their potential toxicity it is important to identify and quantitate the mechanism(s) of formation of particulate sulfate salts.

ACKNOWLEDGMENTS

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Sulfur and Trace Metal Particulate Emissions from Combustion Sources

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ABSTRACT

Oil-fired and coal-fired power plant particulate emissions have been physically and chemically characterized. The concentrations of sulfur and 27 other elements in the samples were determined by high resolution wavelength dispersive X-ray fluorescence analysis (XRF). Particle size distributions were measured with in-stack and extractive cascade impactor arrangements. Elemental particle size distributions were also determined by XRF analysis of sized emissions collected on the impactor stages.

Oil-fired emissions were collected for analysis during eight separate field studies. Three of the studies were conducted at the same plant at three different times. The plant was burning high sulfur oil but with different vanadium contents. The studies conducted at the other five plants included a range in boiler size, in sulfur content in fuel, in trace metal content in fuel, and in level of excess oxygen in the boiler.

Emission samples were collected from five coal-fired power plants, one of which was equipped with flue gas desulfurization (FGD) facilities. Two of the plants were consuming eastern interior coal of high sulfur (3%-5%) content. Two plants were burning a fairly high ash, subbituminous western coal with less than 7.0% sulfur. Emissions from the fifth plant, which was

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equipped with FGD units, were collected from one of the scrubber modules. Sulfur was the most abundant element determined in the particulate emission from the scrubber; reported as sulfate, it was 58%-70% of the total analyzed mass. Analysis of all significant expected companion cations accounted for only about 75% of the total sulfate, which suggests the remainder was sulfuric acid.

INTRODUCTION

The primary objective of a series of investigations conducted by the Particulate Emissions Research Section has been the chemical and physical characterization of particulate emission from oil-fired and coal-fired power plants. Additional objectives of the field studies at these combustion sources have been to evaluate new monitoring instruments and to evaluate sampling techniques used for stationary source testing. These investigations have included field studies at six oil-fired power plants and five coal-fired plants. Emphasis is placed on coal-fired plants in this paper since portions of the oil-fired studies have been previously described (1)(2).

MEASUREMENT PROCEDURES

At each site particulate samples were collected on various filter substrates for chemical analysis of the emissions. Particle sizing samples were collected with cascade impactors and small cyclone samplers. Total particulate mass emission tests were made by Method 5 type procedures. Details of these collection procedures and the analytical methods used for chemical characterization of the samples are presented elsewhere in these proceedings (3). Most of the chemical analyses of the emission samples were by X-ray fluorescence (XRF) spectrometry, so only the elemental composition, not the chemical compounds present, is determined. For example, results are reported for particulate sulfur only as the amount of elemental sulfur. If the sulfur is present as sulfate, the mass of the sulfate would be three times the reported values.

OIL-FIRED POWER PLANTS

Site Descriptions

Characterization studies were conducted at six oil-fired power plants varying in generating capacity, burning fuel with a wide range of sulfur and trace metal contents, operating at different levels of excess oxygen in the boiler, and utilizing fuel additives at various levels. The detailed description of these plants and the operating conditions during the sample collection periods have been previously reported (1). Table 1 is a summary of the important operating parameters of the oil-fired plants and shows the wide variety of conditions which were examined. All sites were operating without emission control devices.

Three sampling trips (A1, A2, and A3) were made to one modern plant that was designed to operate at extremely low excess oxygen levels in the boiler. The fuel being burned had high sulfur content (2.4%) on each occasion, but the vanadium content was different (192 ppm, 593 ppm, and 292 ppm).

Table 1. Operating Conditions at Oil-Fired Power Plants During Testing Periods

Site	Power load (MW)	Excess Oxygen (vol. %)	Fuel Content V (ppm)	Ni (ppm)	S (%)
A1	300-560	0.2-1.2	192	16	2.43
A2	525	0.1-0.7	593	68	2.40
A3	525	0.2-1.1	292	50	2.40
B[a]	127,127,240	1.7,2.0,0.6	192	16	2.43
J	50-60	1.5-1.7	111	14	1.42
M	150-190	3.0-6.0	15	21	1.23
W	600	0.8-2.3	447	62	2.15
N	95	1.5-2.8	113	67	1.74

[a] Three units, each tested twice.

Summary of Results of Oil-Fired Power Plants

Details of some of the earlier results obtained at oil-fired power plants have been previously reported (1)(2); therefore, only the more important general observations are reported here. Of the elements analyzed by XRF, sulfur, vanadium, and nickel were the most predominant. The emission concentrations of vanadium and nickel were directly related to the fuel content of these metals. The particulate sulfur emission levels were more complex, as the concentrations were found to be related to the fuel sulfur content, boiler excess oxygen levels, and the fuel vanadium content. At sites where sampling was made at several excess boiler oxygen levels, the particulate sulfur increased with increased excess oxygen. This is presumably due to greater oxidation of the sulfur to sulfate forms. Carbon content increased as the excess oxygen decreased. At Site A1 carbon was as high as 70% of the total mass at excess oxygen levels of 0.2%. Particle size determinations with both in-stack and extractive cascade impactor arrangements indicated that at all sites most of the particles are less than 0.4 μm in diameter. At Site A1, during operation at low excess oxygen, a second mode around 10 μm was present. These larger particles were highly carbonaceous. Elemental analysis of sized fractions revealed that sulfur was present in the larger size fractions to a greater extent than nickel or vanadium. Most of the nickel and vanadium were associated principally with smaller particles (mass median diameters less than 0.4 μm). Iron, which often originated from corrosion to a greater extent than from the fuel, was associated with the larger particles (mass median diameter about 3 μm).

COAL-FIRED POWER PLANTS

Site Descriptions

Sampling was conducted at five coal-fired power plants that were consuming fuel of widely varying sulfur and mineral concentrations. Four plants had electrostatic precipitator (ESP) control systems. Three of these were sampled from ports in the breeching between the ESP units and the stack; the fourth was sampled from ports in the stack. The control system at the fifth plant consisted of two scrubbers in series, a Venturi scrubber and a flue gas desulfurization (FGD) scrubber. The emissions samples were collected after a FGD unit at this plant. Some of the plants were sampled at various operating conditions, including different excess oxygen levels in the boiler and a variation in the number of ESP fields operating in order to change the particulate emission loading.

Brief descriptions of the five coal-fired plants and operating conditions during the sampling periods follow. Table 2 lists the important operating conditions at each site.

Table 2. Operating Conditions at Coal-Fired Power Plants During Testing Periods

Site	Power (MW)	Coal Type	Coal % S	Coal % Ash	Control System
P	100	Eastern Interior	3.3	8	ESP
L	330	Eastern Interior	3.9	14	ESP
SC	520	Wyoming	0.7	12	ESP
CB	88	Wyoming	0.7	12	ESP
K	720[a]	Western Interior Sub-bituminous	4.8	29	Venturi Scrubber followed by FGD Scrubber

[a] Emissions were sampled from the FGD unit operating at 115 MW.

Site P--This facility was an old, small coal-fired power plant that was burning an eastern interior, high-sulfur coal. The unit sampled had a normal load rating of 100 MW. Sampling ports were located on the outlet breeching of the ESP serving the boiler. The particulate collection efficiency of the ESP was lowered by reducing the number of ESP fields operating.

Site L--This plant had a normal load of 300 MW, was burning a high-sulfur eastern interior coal, and had an ESP that was operated at several efficiency levels during the tests. Samples were taken from ports in the breeching between the ESP and the stack.

Site SC--The unit sampled at this plant had a nominal gross generating output of 520 MW. A very low-sulfur coal (0.7%) that was mined in Wyoming was burned. Particulate emissions were controlled by 32 ESP units. Loading was varied at times by cutting out 8 or 12 units. Sampling ports were located on the stack.

Site CB--This was a small unit, 88 MW nominal output, that was controlled by an ESP. It was burning a Wyoming-mined coal with a nominal sulfur content of less than 0.7%. Particulate loadings were reduced by cutting off some of the ESP fields. Sampling ports were located between the ESP and the stack.

Site K--This plant operated at loads from 300 to 720 MW during the testing periods. Particulate emissions were controlled by eight parallel dual units, a Venturi scrubber and a FGD scrubber in series. Sampling was conducted after the newest and most modern of the FGD units. The unit was operating at a 115 MW load during all of the tests. The boiler was burning a very high-sulfur (4.8%), high-ash western interior sub-bituminous coal.

Particulate Emissions

Total particulate emissions concentrations (milligrams per normal cubic meter, mg/Nm^3), as determined by Method 5 procedures, are listed for Sites P, L, SC, CB, and K in Tables 3 through 7. For the first four sites, which had ESP control systems, the emission values are given for full ESP operation and conditions with some ESP units off. Although cutting off the first one or two ESP fields often did not greatly change the particulate loadings, sufficient units were cut off to obtain significant increases in loading at all but Site CB. The elemental data show drastic compositional changes as the particulate loading is changed by reducing the electrostatic precipitation efficiency.

Elemental Composition

The composition of the particulate emissions from the two high-sulfur ESP controlled plants were analyzed for 28 elements by XRF. The results are listed in Table 8 for Site P and in Table 9 for Site L. These results are presented in percentage of the total analyzed material which does not include elements with atomic numbers less than that of fluorine (9). The composition changes drastically with electrostatic precipitation. For example, at Site P the sulfur was about 70% of the total at normal (full ESP) conditions but only about 5% with two ESP units out. Iron was 8%-12% with normal ESP control but increased to 45%-55% with two units out. The same extreme changes were observed at Site L. Sulfur dropped from 75% of the total analyzed material in samples which passed the fully operating ESP units to less than 6% when ESP units were cut out. Again, the percentage of iron was less in samples that were obtained with the ESP units operating at normal levels.

Table 3. Total Mass and Elemental Particulate Emission Concentrations - Site P

		Concentrations (mg/Nm^3)			
ESP Fields Out		Total Mass	S	V	Fe
0		63	6.1	<0.01	(7.7)*
		72	7.7	<0.01	0.83
		174	7.1	<0.01	0.59
		147			
		108	8.4	<0.01	0.89
		105	13.	<0.01	0.99
	Average:	111	6.9	<0.01	0.82
2		569	3.5	0.35	64.
		422	8.3	0.19	39.
		424	11.0	0.16	33.
		484			
			2.8	0.70	46.
			5.5	0.13	27.
			6.5	0.07	22.
			2.2	0.39	67.
			3.0	0.22	42.
			3.8	0.09	27.
			3.2	0.35	64.
			5.3	0.58	117.
			9.3	0.76	160.
	Average:	475	5.4	0.29	59.
3		1,830			

*Sample was probably contaminated with corrosion products and the value was not included in the average.

Table 4. Total Mass and Elemental Particulate Emission Concentrations - Site L

ESP Fields Out		Concentrations (mg/Nm^3)			
		Total Mass	S	V	Fe
0		107	11	.45	2.9
		291	14	.22	1.2
		461	15	--	1.2
	Average:	286	13	.22	1.8
1		313	16	.93	50.
			16	.64	37.
	Average:	313	16	.79	44.
2		365	13	.80	63.
		461	18	1.8	186.
		900	15	1.0	82.
		950	5.2	1.2	133.
			12	.82	71.
			17	1.0	81.
	Average:	740	14	1.1	103.
3		3,400	--	--	--
		2,100	--	--	--
	Average:	2,700			

Table 5. Total Mass and Elemental Particulate Emission Concentrations - Site CB

		Concentrations (mg/Nm^3)			
ESP Fields Out		Total Mass	S	V	Fe
0		176	0.65	0.03	2.2
			0.96	0.04	3.1
			0.72	0.02	2.0
		98	0.63	0.02	2.5
			0.56	0.02	2.3
			0.62	0.02	2.0
			0.58	0.03	2.0
		66	0.64	0.02	3.6
			0.76	0.03	2.8
			0.69	0.02	2.8
		78	0.69	0.01	2.9
			0.73	0.01	2.5
			0.67	0.01	2.8
	Average:	105	0.68	0.02	2.6
1		83	0.93	0.02	2.7
			0.92	0.01	2.8
			1.07	0.01	2.9
		89	0.82	0.01	3.0
			0.87	--	2.6
			0.85	--	2.2
	Average:	86	0.91	0.01	2.7

Table 6. Total Mass and Elemental Particulate Emission Concentrations - Site SC

ESP Fields Out		Concentrations (mg/Nm^3)			
		Total Mass	S	V	Fe
0		15.3	0.04	--	0.06
			0.05	--	0.06
			0.07	--	0.09
		22.0	0.25	0.008	0.58
			0.21	0.010	0.48
			0.23	--	0.36
	Average:	18.7	0.14	--	0.27
8		23.9	0.33	0.012	0.67
			0.37	0.011	0.70
			0.34	0.010	0.52
			0.34	0.013	0.52
	Average:	23.9	0.34	0.011	0.60
12		88.1	0.74	0.047	3.2
			0.98	0.046	3.4
			1.17	0.057	4.0
			0.90	0.057	3.8
			1.03	0.056	3.8
			1.18	0.059	4.0
			1.24	0.055	4.0
			1.49	0.057	5.4
	Average:	88.1	1.09	0.054	3.9

Table 7. Total Mass and Elemental Particulate Emission Concentrations - Site K FGD Scrubber

	Concentrations (mg/Nm^3)				
	Total Mass	S	Zn	Fe	No. of Tests
	137	21.1	8.1	10.2	8
	123	23.4	5.8	7.7	6
	89	19.6	4.2	8.9	3
	193	32.3	9.4	13.8	3
	175	30.2	12.9	13.7	3
Average:	143	25.3	8.1	10.9	

Table 8. Elemental Composition of Particulate Emissions
Site P
(Percent of Total Amount Analytically Determined)

ESPs Out: Load: Excess O_2:	0 Full Normal	0 Full High	2 Full Normal	2 Half Normal
Element*				
F				
Na			0.07	
Mg	0.22	0.24	0.40	0.52
Al	5.0	6.5	14.	19.
Si	5.8	7.8	16.	22.
P	0.03		0.12	0.13
S	70.	69.	5.7	6.7
Cl				
K	0.25	0.62	3.0	3.2
Ca	0.49	0.38	2.0	1.5
Ti	0.56	0.76	2.7	2.4
V			0.28	0.17
Cr	4.3	2.0	1.3	1.2
Mn	1.4	0.06	0.15	0.14
Fe	8.2	12.	55.	45.
Co			0.16	0.09
Ni			0.10	0.08
Cu	0.18		0.04	
Zn	0.17	0.09	0.45	0.29
As				
Se				
Br	0.42		0.10	0.07
Cd			0.01	0.01
Sn			0.01	
Sb				
Ba	0.06	0.09	0.26	0.18
Hg				
Pb	2.6	0.49	0.45	0.39

*Samples were analyzed for all elements; blank indicates content was below detection limits (3).

Table 9. Elemental Composition of Particulate Emissions
Site L
(Percent of Total Amount Analytically Determined)

ESP Units Out:	0	1	3
Element*			
F			
Na		0.07	
Mg		0.57	
Al	5.6	8.2	17.
Si	8.4	11.	24.
P	0.33	0.25	0.23
S	75.	5.7	5.9
Cl			
K	0.84	3.1	6.1
Ca	2.6	5.0	8.1
Ti	0.61	1.4	2.2
V		0.34	0.38
Cr		0.61	1.5
Mn		0.19	0.26
Fe	6.2	18.	31.
Co		0.03	0.06
Ni		0.03	0.05
Cu		0.06	0.08
Zn	0.11	0.35	0.52
As			
Se			
Br			
Cd		0.01	0.01
Sn		0.07	0.10
Sb			
Ba	0.11	0.13	0.19
Hg			
Pb		0.31	0.46

---

*Samples were analyzed for all elements; blank indicates content was below detection limits (3).

Elemental Emission Concentrations

The particulate concentration (mg/Nm^3) of the elements sulfur, vanadium, and iron in the emissions from plants controlled by ESP are listed in Tables 3 through 6. The concentrations of sulfur, iron, and zinc in the particulate emission from the FGD scrubber at Site K are given in Table 7. For the two plants burning high-sulfur coal and controlled by ESP units, Plants P and L, the sulfur concentration values did not exhibit the extreme increase that was observed with iron and vanadium when the ESP units were cut off. For example, the sulfur concentration at Site L (Table 4) was unchanged, within experimental error, whereas the iron concentration was about 60-fold lower at full ESP operation compared to two units out. Similar results were observed at Site P (Table 3). The sulfur concentrations at Sites SC and CB were very low, principally due to the low sulfur coal being burned. In contrast to the results at the plants burning high-sulfur coal, a significant reduction in the particulate sulfur concentration with an increase in the number of ESP units in operation was observed at Site SC (Table 6). The sulfur concentration emitted from the FGD scrubber at Site K, about 20-30 mg/Nm^3, was the highest of the five sites tested. In the samples from this site, insufficient cations were found to account for all the sulfur when it is assumed to be all sulfate. The results indicate that when all cations are considered to be as sulfate, which is not necessarily the case, 25% of the sulfate is unaccounted for and is probably present as free sulfuric acid. This suggests at least 15 mg/Nm^3 sulfuric acid was being emitted.

Particle Size Distribution

The effect of electrostatic precipitation on the particle size distribution at Sites P and L is shown by the in-stack cascade impactor data in Tables 10 and 11. At Site P the apparent mass median diameter (MMD) when all precipitators were operating was very small. The data from the two in-stack impactor runs indicate the MMD was less than 0.3 μm, as more than 50% of the mass was on the back-up filters. The data from the extractive impactor indicate values of about 0.45 and 0.9 μm for MMD of two runs. This small particle size does not agree with the size distribution data previously reported for other ESP controlled coal-fired plants or with data based on concurrent transmissometer measurements (slope of extinction coefficient versus particulate mass concentration) which indicate that the particles were much larger (4). With two ESP units out at Site P, the MMD was large, about 5-10 μm. At Site L the very fine particles with full ESP operation were not observed.

Table 10. Effect of Electrostatic Precipitation on Particle Size Distribution Site P

		No. of Tests:	1	1	5	1
		Conditions:				
		ESPs Out:	0	0	2	2
		Load:	Full	Full	Full	Half
		Excess O_2:	Normal	High	Normal	Normal
Stage	D_{50} (μm)		(milligrams/normal cubic meter)			
1	23		0.3	1.4	1770.	61.8
2	10		0.3	1.3	1250.	31.1
3	4.7		0.8	3.0	770.	98.6
4	1.9		0.8	4.3	167.	29.6
5	1.0		6.7	1.2	56.	8.8
6	0.52		6.4	0.9	37.1	1.3
7	0.27		7.6	0.9	23.4	0.6
Filter			13.0	12.7	134.5	5.4

Table 11. Effect of Electrostatic Precipitation on Particle Size Distribution
Site L

Stage	D_{50} (μm)						
		No. of Tests:	1	1	1	1	1
		Conditions: ESPs Out:	0	1	2	2	3
		Excess O_2:	Normal	Normal	Normal	High	Normal
			(milligrams/normal cubic meter)				
1	23		1.1	7.2	280.	302.	2820.
2	10		1.5	5.3	295.	148.	1340.
3	4.7		4.4	18.6	84.	89.	600.
4	1.9		5.9	11.7	40.4	36.	220.
5	1.0		3.2	5.0	11.1	13.5	44.2
6	0.52		1.2	1.4	2.5	3.4	12.6
7	0.27		0.9	1.0	1.7	1.3	15.1
Filter			9.3	27.1	15.8	12.8	109.

The particles in the emissions from the FGD unit at Site K had a MMD less than 0.4 μm.

Summary of Results of Coal-Fired Power Plants

A summary of the total mass and the sulfur, iron, vanadium, and zinc elemental concentrations for the five coal-fired power plants at normally controlled conditions is presented in Table 12. The sites (P and L) burning high-sulfur coal emitted fairly high particulate sulfate concentrations, while Sites SC and CB, which were consuming low-sulfur coal, as expected had low particulate sulfur values. At the plants burning high-sulfur coal, the sulfur concentration, in contrast to that of the trace metals such as iron and vanadium, did not change greatly with changes in the number of ESP fields that were operating. These results indicate that the ESP controlled emissions have a higher percent particulate sulfur than uncontrolled emissions. Most of the particulate sulfur emissions from these two plants are apparently in a form that is not efficiently removed by the ESP units. These forms might be fine particles or vapor of sulfuric acid which subsequently condenses or is adsorbed after the material passes through the ESP units.

The highest sulfur concentrations were found at Site K which was sampled after the FGD scrubber. Iron and zinc concentration were also high at this site.

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Table 12. Summary of Emission Concentrations at Coal-Fired Power Plants

Site	Power (MW)	Concentrations (mg/Nm^3)				
		Total Mass	S	V	Fe	Zn
P	100	111	6.9	<0.01	0.8	--
L	330	195	13.0	0.33	1.8	--
SC	520	19	0.14	0.03	2.7	--
CB	88	104	0.68	0.23	2.6	--
K	115	143	25.3	--	10.9	8.1

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Inorganic Compounds Present in Fossil Fuel Fly Ash Emissions

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ABSTRACT

Vast tonnages of fly ash are emitted from coal-fired and oil-fired power plants. Based on elemental analyses, these emissions contain hazardous substances, but full assessments of the health hazards they produce require knowledge of the chemical forms of the largely inorganic emissions.

X-ray diffraction, (subtractive) Fourier Transform Infrared, chemical phase analyses, coupled with extensive elemental determinations and limited equilibrium thermodynamic calculations were applied to a group of samples collected from oil-fired and coal-fired power plant stacks to provide information on the chemical structure of fly ash emissions.

Investigations produced considerable data important in toxicity evaluations. Notably, oil-fired fly ashes contain a highly water-soluble phase, with sulfate as the principal anion component. Vanadium is present largely as a water-soluble vanadium (IV) oxysulfate. Valence state analyses show direct correlations of V (IV) with water solubilities.

Due to the presence of a high concentration insoluble iron aluminum silicate glass phase, water-soluble sulfate compounds are less prominent in coal-fired fly ashes, with a range of up to 30%. Metal oxides also are present in both types of fly ash, but they are not the principal constituents on which toxicity evaluations should be based.

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INTRODUCTION

The literature abounds with analytical methodology descriptions and applications to inorganic particulate pollutant analyses (1-13). The great majority of these publications and references describe and/or are applied to the elemental and anionic contents of pollutant samples.

Comparatively, methods applicable to inorganic compound or chemical form identification and analysis are few, and descriptions of these applied to pollutant samples are quite limited in the literature and in ongoing research and development activities. This lack of attention given to inorganic compound identification in pollutants is unusual in view of frequently declared needs for such information in health and toxicity assessment studies, control measures, and disposal means. Several reasons can be cited for this anomaly, but a principal cause appears to be the relative difficulty of inorganic compound identification of samples as complex and heterogeneous, as are pollutant emission particulates. The commonly and readily used techniques for analysis of inorganic constituents consist of initially breaking samples down to their ionic forms and/or utilizing the atomic characteristics of the samples' constituents and then isolating individual elements, cations, or anions, chemically or spectrally for identification and quantification. This is in contrast with the more commonly used organic species analysis methods such as infrared and mass spectrometry which are based largely on identifications of molecular fragments and thus are relatable more directly to elucidation of organic compound constituents. These, of course, are generalizations; since with selected sample dissolution the valence state of certain elements can be retained and quantified, and certain inorganic species such as alpha quartz, asbestos, etc., have distinctive molecular spectral characteristics and/or specific crystalline forms. However, the use of compound specific techniques for inorganic species identification has not been exploited to any great degree on complex pollutant emission samples. Inorganic compound identification and analyses of pollutant emission samples, what little has been done, has relied mostly on XRD techniques plus morphological characterization of sample by component recognition, using the microscopy-instrumented tools of SEM, STEM, and EMP wherein microscopic viewing can be aided by elemental analyses of the viewed particle or particle groupings. More recently the surface identification techniques of ESCA, Auger, SIMS, etc., have been applied to pollutant particulates, but these techniques are difficult to standardize and to interpret derived data.

More surprising than the dearth of information on the inorganic compound structures of particulates emitted from sources using fossil fuels are the comparatively sparse data available even on the elemental and anionic contents of oil-fired fly ash emissions. Oil-fired power plants still are a major source of electrical energy, especially in the eastern and southern regions of the U.S. Most frequently these plants are operated with little or no emission control equipment. As a result, although fuel oil thermal ash contents range only from 0.05% to 0.2%, the particulate emission rates from oil-fired plants can be high even as compared to rates from the much higher ash content coal-fired sources which are operated with more rigorous control measures. However, literature sources reveal very little concerning even the elemental compositions of particulate emissions from these sources.

Due to the high ash contents of coal fuel sources and the consequent need to find disposal means and/or alternate usages for the high tonnages of collected emission particulates, and to concern over the potential health hazards consequences of these measures, the chemical and physical natures and elemental contents of fly ashes from coal-fired sources have been studied in more detail than have those from oil-fired sources. However, until recently even these studies have not focused primarily on methodologies to determine the inorganic compound forms present in fossil fuel particulate emissions. It should be pointed out that both oil-fired and coal-fired fly ashes contain <0.1% organics, as based on $MeCl_2$ extractions, so the particulates emitted as fly ashes are primarily inorganic in form.

In summary, in view of the vast tonnages of fly ashes emitted from oil-fired and coal-fired power plants and other sources using or processing fossil fuels and the increased concerns of the potential health hazards of these due to the use of additional and dirtier fossil fuel sources, there exists a need for methodologies to identify and quantify the chemical structure of the emissions which are largely inorganic. The work described herein was performed to help fill the information gap caused primarily by lack of existing methodology. The work is ongoing and has been directed mostly toward oil-fired fuel emissions since these are the least known chemically and may pose the greatest health hazards.

EXPERIMENTAL

The techniques considered most applicable to complex pollutant particulate samples are listed in Table 1.

The first three techniques listed in Table 1, coupled with detailed cation and anion determinations and limited equilibrium thermodynamic evaluations of the chemical data, provided most of the data presently obtained on the inorganic constitution of oil-fired and coal-fired fly ash samples.

Table 1. Analytical Techniques Applicable to Inorganic Compound Identification

Techniques	Comments
X-ray Diffraction	Components must have crystalline structures.
Chemical Phase	Valence state measurements and component separations and analyses.
Fourier Transform Infrared	Application to inorganic compounds is a new development.
Thermal	TGA, DTA, DSCA, calorimetry
Microscopy - optical, petrographic, chemical, scanning electron, scanning electron transmission, and electron microprobe	Except for the petrographic and chemical methods, the identification of compounds is by elemental association within particles.
Surface Methods	ESCA, Auger, SIMS, IMA
Mass Spectrometry	Knudsen cell and possibly high resolution mass spectrography.
X-ray Emission Spectrometry	Wavelength peak shifts due to chemical bonds show various oxidation states.

The experimental efforts were directed principally toward the investigation and use of techniques better established in their development and application to inorganic compound identification and quantitation than are techniques such as ESCA, SIMS, and IMA. This selection was guided by the need to fill the large data gap existing as to the total chemical constitution of fossil fuel particulate emissions. An exception to this technique selection process was the exploration and use of FT-IR for inorganic compound identification.

Field Sample Collections

Samples of oil-fired and coal-fired fly ashes were collected from several power plant sites which burn fossil fuels of various origins with the objective of obtaining a range of fly ash sample compositions which would be representative of present power production processes. Sampling was performed at the port holes in the stacks beyond any emission control process operation. The fly ash samples were obtained by simply inserting a 2-cm-diameter glass-lined probe into the center of the stack perpendicular to the stack stream flow and, with a 1-hp blower, drawing a portion of the flow into a fine mesh Teflon bag. A 24-hour sampling time period usually provided 50 to 75 grams of stack emission particulates. At the conclusion of the sampling period the Teflon bag was removed from the Hi-Vol container, sealed in a polyethylene bag, and returned to the laboratory for analyses of the collected particulates. No efforts were made to relate the samples with combustion conditions, to sample isokinetically, or to separate aqueous phase emissions from the particulates. The objective of the sampling was to obtain relatively large masses of samples for purposes of methodology development with the expectation that the developed methodologies can be applied to more carefully planned sampling efforts at a later time.

Sample pretreatment was considered in carrying out the analyses of fossil fuel particulate emissions samples since unknown alterations of their chemical forms must be avoided. Samples collected in the way described from stack exit flues at temperatures of about 150°C do contain a lot of moisture, and pretreatments such as desiccation and heating can alter the sample weight and chemical forms. From structural, crystallographic and/or optical--XRD, IR, petrography--analytical aspects, it is desirable to work with samples in a stable, moisture-free condition, since the presence of loose and even bound forms of water complexes the identification efforts. A common practice of drying samples at 105°C before bottling, weighing, and analysis is not applicable to the wet particulate emissions since for many samples there is no point where loose, unbound, capillary water only is removed by heating in air atmosphere. This is illustrated by the data given in Table 2 for samples collected at the stack exit ports of coal-fired and oil-fired power plants. Thermograms of a composite of four oil fly ash samples (equal amounts of each mixed together) heated slowly at 1°C per minute in air and in argon are shown in Figure 1. The thermogram for the oil-fired fly ash composite heated in air shows a continuous weight loss over a 15-hour heating increase at a 1°C per minute change. The sequence of weight losses, as shown by individual sample TGA and DTA plots in air, indicates capillary or unbound water, hydrated or bound water, carbon, and the partial $SO_4^=$ losses.

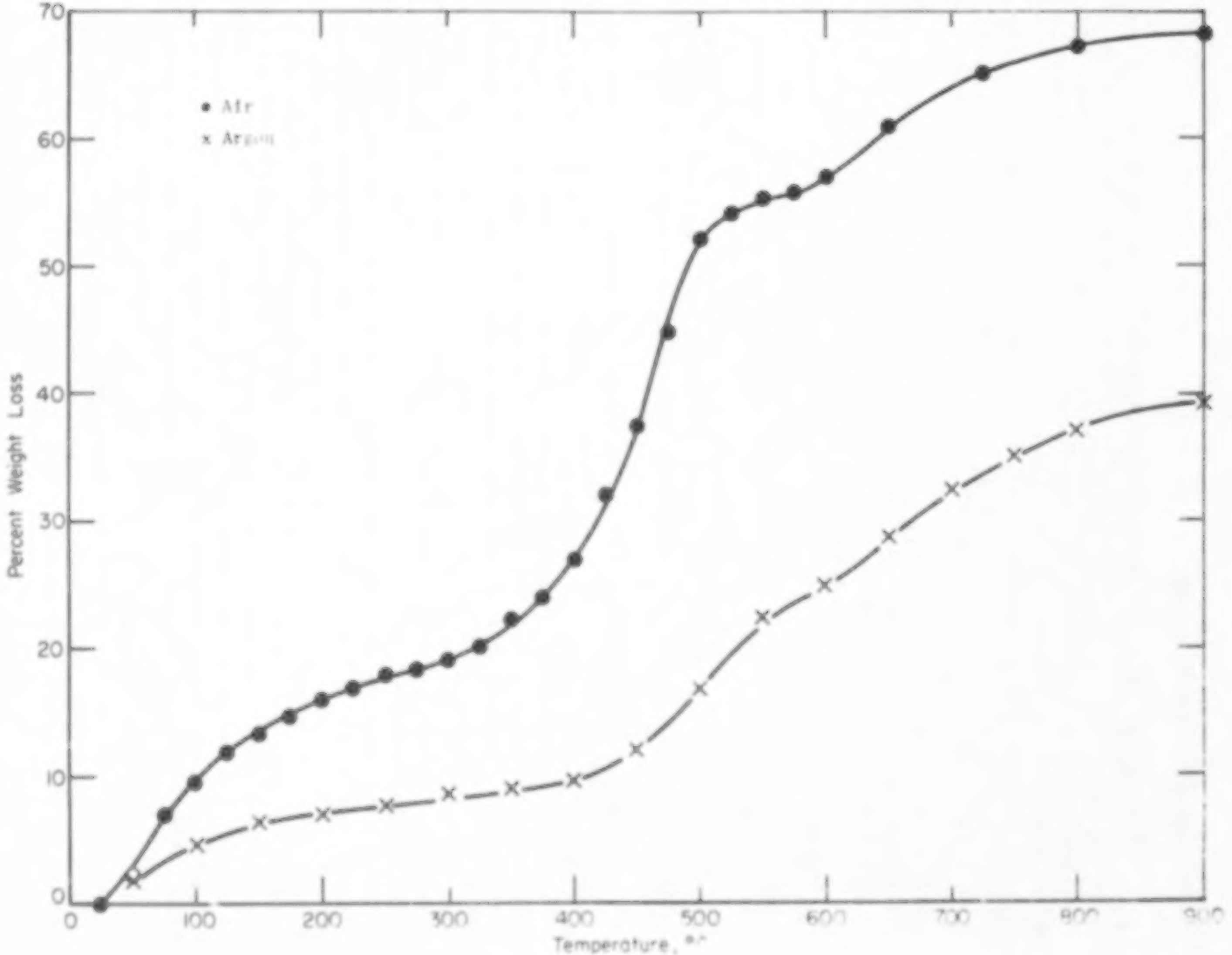
70
60
50
40
30
20
10
0
Percent Weight Loss
0
100
200
300
400
500
600
700
800
900
Temperature, °C
● Air
× Argon

Table 2. Weight Losses of Fly Ash Samples on Slow Heating in Air (in Percent)

	105°C	200°C	400°C	750°C
Oil Fly Ash No. 1	2.4	4.5	18.0	22.5
Oil Fly Ash No. 2	3.0	4.8	69.5	74.0
Oil Fly Ash No. 4	4.5	12.5	28.0	57.0
Oil Fly Ash No. 5	5.05	10.6	36.9	45.5
Coal Fly Ash NBS	0.25	0.55	1.1	4.1
Coal Fly Ash No. 1	1.0	1.8	2.6	4.7
Coal Fly Ash No. 2	4.0	5.4	13.0	19.2
Coal Fly Ash No. 3	4.0	6.5	9.0	24.2

Thermograms based on heating the samples under argon show minor incremental weight changes between 200°C and 400°C, as illustrated by the composite sample in Figure 1, indicating probable loss of most unbound water contents. IR and XRD spectral and pattern images obtained on the samples after heating under argon are much improved, as are the microscopic appearances of viewed sample particle fields. Based on these findings, heating the samples under argon appears to be a reasonably satisfactory mode of removing the unbound water without altering otherwise the integrity of the sample structure. Based on individual thermograms for each sample, heating samples at 350°C under argon was adapted as the preparation mode for IR, XRD, and microscopic examinations. Other determinations were carried out on air-dried samples.

Six oil-fired and four coal-fired fly ash samples have been used to date for the methodology development work. The NBS Standard Reference Material Coal Fly Ash is actually a group of precipitator and mechanically collected ashes which have been sieved and blended prior to standardization. It is planned to add two Western coal-fired fly ashes to the experimental samples. The analyses of the fuels being burned at the times of sample collections are given in Table 3.

ELEMENTAL ANALYSES

Inorganic compound identification can be aided considerably by knowledge of the elemental constituents of samples so complete analyses of the work samples were obtained as shown in Tables 4 and 5. Significant data to note in Table 4 are:

Table 3. Analyses of Fuels Used During Collections of the Fly Ash Samples[a] - Results in PPM Except Where Percent Is Given

	Fuel Oils				Coals	
	No. 2	No. 4	No. 5	No. 6	No. 2	No. 3
S	2.5%	2.15%	2.65%	1.56%	3.87%	3.62
V	540	446	292	40	--	--
Ni	69	62	50	20	--	--
Fe	5	45	17	15	1.0	0.9
Mg	139	6	114	1490	0.02%	0.1
Al	2	2	1	60	1.3%	1.0
Si	5	3	4	10	1.0%	1.7
Ca	10	5	7	5	0.2%	0.3
Na	20	10	159	8	--	--
K	4	4	7	6	--	--
Ash at 550°C	0.18%	0.10%	0.14%	0.15%	8.2%	14.4%

[a] No fuel oil sample was available for the No. 1 fly ash. Fly ash No. 1 was on hand from a 1973 research program taken from a power source purportedly using a domestic origin No. 6 fuel oil.

The No. 3 fuel oil and fly ash samples were taken about 1 month later from the same power source as the No. 2 and are nearly identical with those of the No. 2.

No coal sample was available for the No. 1 coal fly ash - the fly ash was on hand from a previous program.

Table 4. Oil-Fired and Coal-Fired Fly Ash Compositions - Major Constituents (Percent)

		C	H	N	$NO_3^=$	NO_2^-	NH_4^+	$SO_4^=$	SO_3^-	$S^=$	Cl	P	Si
Oil-Fired Fly Ashes													
No. 1	Total Sample Content	12.4	0.9	0.1	0.005	<0.01	0.012	36.9	<0.01	<0.01	0.05	0.008	0.31
	Water-Soluble Content							36.0	"	"			<0.01
	Water-Insoluble Content							0.9	"	"			0.31
No. 2	Total Sample Content	69.0	0.7	0.9	0.013	0.005	0.13	12.0	"	"	0.02	0.002	0.2
	Water-Soluble Content							12.0	"	"			<0.01
	Water-Insoluble Content							0.15	"	"			0.2
No. 4	Total Sample Content	21.5	1.0	0.9	0.02	0.01	0.81	41.2	"	"	0.02	0.004	0.2
	Water-Soluble Content							41.1	"	"			<0.01
	Water-Insoluble Content							0.1	"	"			0.2
No. 5	Total Sample Content	1.5	1.2	0.1	0.02	<0.01	0.16	57.6	"	"	0.05	0.001	0.05
	Water-Soluble Content							58.6	"	"			<0.01
	Water-Insoluble Content							0	"	"			0.05
No. 6	Total Sample Content	14.5	2.4	6.5	<0.01	0.03	7.3	49.2	"	"	0.06	0.05	0.22
	Water-Soluble Content							48.4	"	"			<0.01
	Water-Insoluble Content							0.8	"	"			0.22
Coal-Fired Fly Ashes													
NBS	SRM 1633 Total Sample	3.3	0.1	<0.1	<0.01	<0.01	<0.01	0.98	"	"	0.005	0.12	20.9
	Water-Soluble Content							0.60	"	"			
	Water-Insoluble Content												
No. 1	Total Sample Content	1.7	0.3	<0.1	<0.01	<0.01	<0.01	3.05	"	"	<0.003	0.14	19.7
	Water-Soluble Content							2.13	"	"			
	Water-Insoluble Content												
No. 2	Total Sample Content	7.0	0.5	0.1	<0.01	<0.01	0.06	6.9	"	"	0.007	0.02	16.7
	Water-Soluble Content							5.75	"	"			
	Water-Insoluble Content												
No. 3	Total Sample Content	0.5	0.7	<0.1	0.02	<0.01	0.01	22.1	"	"	0.05	0.08	16.6
	Water-Soluble Content							19.6	"	"			
	Water-Insoluble Content												

(Continued)

Table 4. (Continued)

		Al	Fe	Ni	V	Mg	Ca	Na	K	Total Organics	Water Solubility	H_2O	H_2SO_4	pH
Oil-Fired Fly Ashes														
No. 1	Total Sample Content	1.25	0.61	1.66	2.27	18.4	1.0	3.91	0.13	<0.1	58.0	7.0	<0.1	3.9
	Water-Soluble Content	0.5	0.30	1.0	0.50	4.71	0.6	3.90	0.13					
	Water-Insoluble Content	0.75	0.31	0.66	1.77	13.7	0.4	0.01	0					
No. 2	Total Sample Content	0.05	0.40	0.85	6.68	3.41	0.31	0.30	0.1		23.3	5.0	0.2	2.7
	Water-Soluble Content	0.02	0.25	0.60	2.23	1.15	0.15	0.30	0.1					
	Water-Insoluble Content	0.03	0.15	0.25	4.45	2.26	0.16	0	0					
No. 4	Total Sample Content	0.40	0.41	1.29	10.2	5.94	0.1	0.50	0.10	0.053	72.0	4.5	0.04	2.42
	Water-Soluble Content	0.23	0.20	1.06	8.98	5.0	0.07	0.51	0.12					
	Water-Insoluble Content	0.17	0.21	0.23	1.22	0.94	0.03	0	0					
No. 5	Total Sample Content	0.01	0.48	2.28	12.85	2.60	0.20	2.02	0.10	<0.1	98.5	5.5	1.0	2.15
	Water-Soluble Content	<0.01	0.49	2.31	12.9	2.65	0.19	2.0	0.09					
	Water-Insoluble Content	0.01	0	0	0	0	0.01	0	0					
No. 6	Total Sample Content	1.42	0.40	0.35	1.10	2.4	0.32	0.20	0.12	<0.1	83.0	2.1	1.5	2.22
	Water-Soluble Content	0.27	0.43	0.30	0.78	2.4	0.16	0.21	0.11					
	Water-Insoluble Content	1.15	0	0.05	0.32	0	0.16	0	0					
Coal-Fired Fly Ashes														
NBS	SRM 1633 Total Sample	12.7	6.5	0.01	0.02	2.0	4.2	0.30	1.75	<0.1	3.5	0.3	<0.1	11.35
	Water-Soluble Content													
	Water-Insoluble Content													
No. 1	Total Sample Content	11.3	12.6	0.06	0.02	0.52	1.5	0.60	1.54	0.04	5.3	1.0	<0.1	4.50
	Water-Soluble Content													
	Water-Insoluble Content													
No. 2	Total Sample Content	10.9	14.1	0.02	0.03	0.2	0.40	0.05	1.0	0.072	13.0	4.0	2.0	3.17
	Water-Soluble Content	0.63	0.56	0.01	0.01	0.01	0.18	0.03	0.5					
	Water-Insoluble Content	10.27	13.54	0.01	0.02	0.01	0.22	0.02	0.5					
No. 3	Total Sample Content	8.79	7.90	0.06	0.06	0.6	3.0	0.08	1.1	0.11	34.0	5.0	2.1	2.73
	Water-Soluble Content	1.63	1.94	0.04	0.04	0.2	1.8	0.06	0.6					
	Water-Insoluble Content	7.16	5.96	0.02	0.02	0.4	1.2	0.02	0.5					

Table 5. Oil-Fired and Coal-Fired Fly Ash Compositions - Trace Constituents

Element	Oil-Fired Fly Ashes					Coal-Fired Fly Ashes			
	No. 1	No. 2	No. 4	No. 5	No. 6	NBS	No. 1	No. 2	No. 3
Li	0.5	0.5	0.2	3.	100.	300.	0.1	200.	200.
Be	0.05	0.3	0.2	0.3	0.1	5.	0.5	1.5	1.5
B	30.	0.5	5.	3.	1.	100.	100.	300.	200.
F	2.	<1.	3.	5.	<1.	10.	20.	30.	60.
Sc	1.	<1.	5.	3.	<1.	20.	10.	30.	40.
Ti	500.	300.	400.	400.	700.	6000.	2000.	100.	3000.
Cr	100.	500.	1000.	500.	450.	130.	100.	150.	1000.
Mn	200.	200.	200.	500.	300.	500.	50.	300.	200.
Co	500.	50.	200.	300.	300.	50.	5.	70.	30.
Cu	500.	100.	200.	400.	400.	120.	30.	200.	300.
Zn	40.	40.	200.	400.	200.	200.	20.	800.	1200.
Ga	5.	5.	50.	60.	40.	50.	10.	100.	60.
Ge	10.	1.	10.	10.	7.	20.	10.	70.	70.
As	30.	20.	30.	30.	20.	60.	20.	100.	100.
Se	7.	5.	10.	3.	7.	10.	5.	20.	20.
Br	10.	3.	25.	25.	2.	10.	15.	5.	20.
Rb	5.	1.	5.	4.	7.	150.	5.	400.	700.
Sr	500.	100.	300.	300.	200.	1500	2000.	200.	150.
Y	50.	3.	5.	10.	10.	30.	50.	100.	30.
Zr	50.	5.	20.	20.	10.	200.	100.	200.	50.
Nb	10.	2.	1.	1.	2.	7.	5.	10.	7.
Mo	100.	50.	100.	100.	150.	20.	10.	40.	70.
Ru	<1.	<1.	<1.	<1.	<1.	<0.5	<0.5	<0.5	<0.5
Rh	<1.	<1.	<1.	<1.	<1.	<0.5	<1.	<0.5	<0.5
Pd	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.
Ag	<1.	<1.	<1.	<1.	<1.	<0.5	<1.	0.7	0.7
Cd	1.	1.5	4.	3.	4.	15.	2.	8.	10.
In	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sn	20.	3.	5.	5.	3.	3.	3.	10.	10.
Sb	3.	5.	10.	10.	150.	7.	1.	10.	15.
Te	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
I	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cs	<1.	<1.	<2.	3.	1.	10.	1.	20.	40.
Ba	1000.	200.	200.	1000.	1000.	2500.	1000.	1000.	500.
La	40.	10.	50.	50.	150.	70.	40.	60.	30.
Ce	50.	5.	25.	30.	100.	125.	75.	100.	30.
59-71	120.	15.	70.	60.	90.	90.	40.	130.	60.
Hf	<0.5	<0.5	<0.5	<0.5	<0.5	10.	3.	2.	2.
Ta	<1.	<1.	<1.	<1.	1.	2.	<1.	1.	1.
W	<1.	<1.	2.	2.	2.	5.	<1.	4.	4.
Re	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Os	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Ir	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pt	0.3	0.3	<0.3	<0.3	<0.4	0.4	0.3	0.4	0.4
Au	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Hg	<1.	<1.	<1.	<1.	<1.	0.1	<1.	<1.	1.
Tl	10.	<0.2	0.5	1.	0.2	2.	2.	15.	30.
Pb	3000.	200.	400.	400.	300.	80.	200.	150.	100.
Bi	<0.1	<0.1	<0.1	0.3	<0.1	0.7	<0.1	0.7	1.
Th	10.	5.	6.	4.	2.	20.	10.	40.	20.
U	10.	5.	2.	10.	2.	15.	10.	40.	30.

(a) There are high concentrations of $SO_4^=$ in the samples.

(b) The $SO_4^=$ is nearly entirely water soluble.

(c) The $SO_4^=$ is essentially the only anion in the water-soluble phase.

(d) There are very high water solubilities of the oil-fired emissions and, to a lesser extent, the coal-fired emissions.

As can be seen, the coal-fired fly ash samples are much less water soluble than are the oil-fired fly ashes, but as is discussed later, the coal fly ash particulates predominantly are amorphous aluminum-iron-silicate glasses which of course, are insoluble. The chemical inertness of these glasses may have favorable health aspects since they contain portions of trace heavy elements which generally are regarded as hazardous. However, the $SO_4^=$ contents of the coal-fired fly ashes are nearly entirely water-soluble. Extensive determinations made on these samples show the sulfur contents to be nearly entirely in the $SO_4^=$ form.

Water-Phase Separation

The above findings suggest a ready, simple mode of fractionating fossil fuel particulate emissions into water-soluble metal (and ammonium) sulfates and water-insoluble metal oxides (and silicates) plus inert carbon. Any free H_2SO_4 acid, of course, also is contained in the water-soluble phase of the samples, but H_2SO_4 acid has not been found to be present in large percentages, although the method used for its determination has given erratic results.

The separation of samples into water-soluble/insoluble phases has proved useful for structural identifications of specific metal sulfate forms, principally by FT-IR, and of oxide forms by XRD.

The water solubility separation is simply achieved by stirring a 2-gram sample in 150 ml of water at room temperature for one hour using a mechanical ("Mag-Mix") stirrer, filtering, washing and drying the insoluble phase, and gently taking to dryness an aliquot of the soluble phase. After drying, the insoluble residue is weighed to give the percent insoluble fraction with the percent soluble obtained by difference. As stated earlier, the only anion of any significant concentration in the concentration in the soluble phase is the $SO_4^=$ and, in fact, the soluble phase contains nearly all of the $SO_4^=$ present in the total unfractionated oil-fired fly ash samples.

In the oil-fired fly ash work samples used in this program, the water-soluble phase represents from 66% to nearly 100% of the sample components exclusive of the inert, soot-like carbon. The soluble phase components of the oil fly ashes are primarily metal and NH_4^+ sulfates plus any H_2SO_4 acid, while the insoluble phase components are carbon, oxides, and minor amounts of insoluble sulfates.

The coal-fired fly ash samples also contain a water-soluble sulfate phase. These are much lower in percentage contents due to the high concentrations of insoluble inert iron-aluminum silicates and lesser amounts of insoluble crystalline minerals such as quartz, hematite, and magnetite in the coal fly ashes.

Oil-Fired Fly Ash Compound Identification

Chemical Valence of Vanadium--In conjunction with the water solubility studies, it was determined that vanadium in the oil fly ash samples is present, principally in a water-soluble form. It was noted that the water-soluble solutions had a greenish to greenish-blue color nearly proportional to the concentrations of vanadium determined present. Valence state measurements of vanadium in the oil fly ash samples were made using an adaptation of an extraction-photometric method described by Shcherbakova, et al. (14), for the determinations of V^V and V^{IV} (actually reduced vanadium) in vanadium catalyst samples. V^V was determined in the presence of V^{IV} at an acidity of 0.2 N since it was determined that at pH ≥ 1 vanadium (IV) is oxidized to vanadium (V) by atmospheric oxygen.

Following the procedure described by Shcherbakova, et al., 0.1 gram of oil fly ash sample was dissolved in 10 ml of 0.2 N HCl, and the insoluble portion was filtered and washed with 0.2 N HCl and diluted to a volume of 100 ml. Extraction was carried out on a 2-ml aliquot using 5 ml of 10^{-2} PMBP solution (1-phenyl-3 methyl-4 benzoyl-pyrazolone-5), 1 ml pentanol, 4 ml chloroform, and 8 ml 0.2 N HCl. V^V in the presence of any reduced vanadium was read spectrometrically at 500 nm. Total V in the sample was determined by oxidizing another aliquot of the above sample solution to V^V and repeating the extraction-photometric procedure. Reduced vanadium was found by the difference between the total vanadium determination result, and the V^V value was determined in the presence of reduced vanadium. Total vanadium in the sample and in the water-soluble phase also was determined by atomic absorption analyses with better precision and accuracy than obtained by use of the extraction-photometric procedure.

The results obtained on the oil fly ash samples by use of the above methods are given in Table 6. As can be seen in the table, the reduced vanadium values (Column 6) coincide closely with total vanadium contents of the water-soluble fraction (Column 5). Since V^{II} and V^{III} vanadium states are very unstable, it is highly probable that the water-soluble vanadium is in the V^{IV} state.

Table 6. V^V in the Presence of Reduced Vanadium and Total Vanadium Determinations (Oil-Fired Fly Ash)[a]

Sample No.	Extraction-Photometric		Atomic Absorption		
	V^V [b]	V^{Total} [c]	V^{Total}	$V^{Water\text{-}Soluble}$	$V^{Reduced}$ [d]
1	1.70	2.25	2.27	0.50	0.57
2	4.50	5.7	6.68	2.23	2.18
4	0.90	10.7	10.2	8.98	9.3
5	0.14	11.75	12.85	12.90	12.71
6	0.35	1.1	1.10	0.78	0.75

[a] Results in percent.

[b] V^V in presence of reduced vanadium.

[c] V^V after oxidation of reduced vanadium.

[d] Difference between Column 1 (V^V in presence of reduced vanadium) and Column 4 (total V determined by AAS) results.

The water solubilities of two reference vanadium compounds (ICN Pharmaceuticals vanadium sulfate and Alfa vanadium oxysulfate) were compared with oil fly ash samples Nos. 2, 4, and 5 before and after heating under argon at 350°C. The vanadium sulfate was found to be very water insoluble both before and after heating. The $VOSO_4 \cdot 5H_2O$ was found to be highly water soluble before heating, exhibiting a deep greenish-blue color but was only very slightly water soluble after heating. (Anhydrous $VOSO_4$ is reported as insoluble in the literature.) The oil fly ash samples behaved similarly with the unheated samples giving deep greenish coloration in the water solutions and the heated samples imparting no color. Semiquantitative analyses of the two reference vanadium compounds and fly ash samples showed no vanadium (<0.1%) was dissolved in water after the samples had been heated.

Based on the valence state determinations, the water solubility color tests, and chemical assays, it appears that the oil fly ash samples contain water-soluble $V^{IV}OSO_4 \cdot 5H_2O$ and water-insoluble V_2O_5.

Using the elemental analyses from Tables 4 and 5, the data given in Table 7 for oil-fired fly ash samples were calculated based on the assumptions that:

(1) The cation concentrations contained in the soluble fractions probably were sulfate forms, since no other anions of any significant concentrations were present.

(2) The cation concentrations contained in the insoluble fractions were oxide forms primarily, plus limited concentrations of insoluble sulfates.

(3) The carbon, of course, would be present as an insoluble form.

For example, considering the Mg in Sample No. 1, of the 18.1% present in the total sample, 4.71% is contained in the soluble phase and the remaining 13.7% in the insoluble phase. Using the gravimetric factor for $Mg \rightarrow MgSO_4$ of 4.95, the $MgSO_4$ content would be

$$4.95 \times 4.71\% = 23.3\% \ MgSO_4 .$$

Similarly, using the gravimetric factor for $Mg \rightarrow MgO$ of 1.66 x 13.7%, the calculated insoluble MgO would be 22.8%.

These assumptions are not at odds with equilibrium thermodynamic calculations. As can be seen in Table 7, the possible calculated combinations total close to 100% for the Nos. 1, 2, 4, and 5 samples. The No. 6 combinations total only ~90%. The total $SO_4^=$ contents of the calculated compounds given at the bottom of Table 6 check reasonably well with determined concentrations given in Table 3 except for the No. 5 sample where the calculated $SO_4^=$ totals 46.5% versus the determined value of 57.6%, and for the No. 6 sample where the calculated $SO_4^=$ totals 55.2% versus the determined value of ~49%.

X-ray Diffraction of Oil-Fired Fly Ashes--Samples were prepared for X-ray diffraction analyses by heating in an argon atmosphere at 350°C for two hours to drive off loosely bound and capillary water, mixing in a mechanical shaker to break up agglomerated particles, and storing in a desiccator prior to X-ray analysis. The total samples, water-soluble and water-insoluble fractions, were

Table 7. Possible Compound Compositions of Oil-Fired Fly Ash Samples Based on Chemical Analyses of Soluble and Insoluble Phases

Calculated Species	No. 1	No. 2	No. 4	No. 5	No. 6
C as C	12.4	63.7	21.5	1.5	14.5
H_2O*	7.0	5.0	4.5	5.5	2.0
H_2SO_4*	0.1	0.2	0.05	1.0	1.5
NH_4 as $(NH_4)HSO_4$	0.08	0.83	5.18	1.03	46.6
Mg as MgO	22.8	3.8	1.6	0	0
Mg as $MgSO_4$	23.3	5.7	24.8	12.9	11.9
V as V_2O_5	3.2	7.9	2.2	0	0.6
V as $VOSO_4 \cdot 5H_2O$	2.5	11.1	44.5	64.0	3.9
Fe as Fe_2O_3	0.45	0.2	0.3	0	0
Fe as $FeSO_4$	0.8	0.7	0.5	1.3	1.1
Ni as NiO	0.85	0.3	0.3	0	0.06
Ni as $NiSO_4$	2.65	1.6	2.8	6.0	0.8
Al as Al_2O_3	1.4	0.06	0.3	0.02	2.2
Al as $Al_2(SO_4)_3$	3.2	0.15	1.45	0	1.7
Si as SiO_2	0.55	0.4	0.45	0.05	0.5
Na as Na_2SO_4	12.1	0.95	1.55	6.25	0.6
K as K_2SO_4	0.3	0.2	0.2	0.2	0.25
Ca as CaO	0.55	0.2	0.04	0.01	0.2
Ca as $CaSO_4$	2.0	0.5	0.25	0.65	0.55
Other Elements as Oxides/Sulfates	1.3	0.35	0.75	1.0	1.0
Totals of Above	97.5	104.2	113.1	101.3	90.1
Sulfates**	35.15	12.3	46.0	46.0	55.2

*H_2O and H_2SO_4 values are those determined as given in Table 4 rather than calculated values based on H.

**$SO_4^{=}$ contents of the calculated species.

run separately. The prepared sample specimens were placed in cavity mounts and analyzed using a Norelco-Phillips X-ray unit, with CuK radiation and a graphite monochrometer. Strip chart recordings were obtained over a 2 θ range of 10°C to 70°C. Structural interpretations were made by use of ASTM reference data plus synthetic standards and reference compounds. Peak heights were read from the strip chart recordings for intercomparisons of sample and sample fraction peak heights with each other and with reference intensities.

As anticipated, the X-ray patterns were very complex due to the numerous phases present and their variances in contained waters of hydration. Interpretations were assisted materially by use of reference patterns obtained on chemical forms postulated as present based on the chemical analyses of the total samples and of their water-soluble and insoluble fractions.

These calculated chemical forms proved useful for both the XRD identifications and the subtractive FT-IR work described later. MgO, V_2O_5, and carbon patterns were readily identified in the total samples and in the insoluble fractions of these in, semiquantitatively, the concentration ranges given in Table 7. No V_2O_5 or MgO patterns were obtained in the No. 5 and No. 6 oil-fired fly ash samples.

XRD patterns were obtained on the vanadium sulfate and oxysulfate reference salts after baking at 350°C under argon and compared with patterns obtained on the total samples and soluble phases of oil fly ashes. Diffraction peaks were obtained on the total samples and water-soluble phases at the d-spacings obtained for the vanadium oxysulfate reference but not the vanadium sulfate. Assays made of the vanadium oxysulfate reference salt indicated a $VOSO_4 \cdot 1H_2O$ composition after baking and $VOSO_4 \cdot 5H_2O$ in the untreated salt. The XRD work is continuing to identify other sulfate and oxide phases present in the samples using an internal standard (NaCl) to quantify the data.

Fourier Transform Infrared (FT-IR)--Based on present investigations, it appears that Fourier Transform infrared spectrometry offers greater potential for inorganic compound identification in complex mixtures than does XRD. While in the past infrared spectroscopy has been used mostly for organic compound identifications, by using the sensitivity of the Fourier Transform infrared system and the data handling capability of a dedicated computer, it has been found that inorganic compounds can be identified as well. The dedicated computer permits the storage of infrared reference compound spectra, identified via elemental--anion/cation--analyses as possibly present on the samples to be examined, and the subtraction of these spectra from unknown sample spectra.

The details of this new application of infrared to oil-fired and coal-fired fly ash samples are given in another paper (15) in this program.

Coal-Fired Fly Ashes

Lesser efforts have been expended to date on coal-fired fly ash inorganic compound identifications. Petrographic examinations and X-ray diffraction analyses have been made which confirm the conclusions of previous investigators (16-20) that coal-fired fly ashes are composed principally of an amorphous glass structure. Water extractions have shown the presence of a water-soluble phase composed principally of sulfates. However, due to the presence of the high concentration glass phase in coal-fired fly ashes, the water-soluble phase is less than in oil-fired fly ashes.

To identify the glassy phase constituents, two synthetic oxide mixtures, G-1 and G-2, were prepared for use as XRD and FT-IR reference materials. Aluminum, iron and silicon oxides were mixed and ground together in the proportions given below:

Al_2O_3 - 51%	Al_2O_3 - 40%
Fe_2O_3 - 20%	Fe_2O_3 - 15%
SiO_2 - 29%	SiO_2 - 45%

Portions of these mixes were then fired to obtain liquid melts, and after quenching and solidification, the melts were ground to ~300 mesh. XRD patterns were obtained on the synthetic oxide mixes, the oxide melts, the coal-fired fly ash total samples, and their water-insoluble fractions. The resultant XRD patterns of the synthetic oxide mix, before melting, showed very strong Al_2O_3, Fe_2O_3, and SiO_2 structures. The oxide melts showed only a weak α quartz, Fe_2O_3, and very weak Fe_3O_4 and Al_2O_3 patterns. X-ray pattern structures found in the coal-fired fly ash samples and in the insoluble phases thereof resembled those of the oxide melts in respect to the strengths of the α SiO_2, Fe_2O_3, Fe_3O_4, and Al_2O_3 patterns. Some additional but weak patterns also were found present in the total fly ash samples but not in the water-insoluble phases.

Only limited additional XRD work is planned on the coal-fired fly ashes since, except for the few metal sulfate and weak oxide patterns which can be seen, the coal-fired fly ashes exhibit little XRD pattern structure. Thus the presence of a large amorphous glass phase is indicated only indirectly by XRD by the absence of strong diffraction patterns.

FT-IR spectra of the glassy or amorphous phase, while strikingly different from spectra obtained of crystalline oxides, appear to be sufficiently unique and definitive for direct identification using appropriately prepared reference materials and spectral subtractions. The water-soluble phases of the coal fly ash samples--sulfates--can be determined by FT-IR similarly to the oil-fired fly ash identifications. At this point, pending further method development to ascertain sensitivity and accuracy, the FT-IR technique appears superior to XRD in identifying the glass phase and metal sulfate constituents of coal-fired fly ashes.

Distribution of Selected Trace Metals in Fly Ash Samples -- Since health effect aspects of fly ash emissions are of key interest, and certain trace elements are suspected to be hazardous, the water-soluble and water-insoluble phases of the Nos. 2 and 3 coal-fired fly ashes were analyzed using spark source mass spectrography. If the trace elements were found to be tied up in the glass phases of the fly ash emissions, it might be presumed that their toxicity effects would be less than if present in a water-soluble form. The results obtained are shown in Table 8.

Table 8. Ratios of Water-Soluble to Water-Insoluble Trace Element Concentrations in Coal Fly Ash

Element	No. 2 Coal Fly Ash	No. 3 Coal Fly Ash
Be	1-1	4-1
V	1-2	2-1
Cr	1-1	1-1
Mn	1-1	1-1
Co	1-2	1-1
Ni	1-1	2-1
Cu	1-1	5-1
Zn	2-1	5-1
As	1-1	3-1
Se	1-4	4-1
Mo	1-1	4-1
Cd	5-1	5-1
Sn	1-5	1-2
Sb	1-5	1-2
Tl	1-1	10-1
Pb	1-1	5-1
U	1-2	1-1

In viewing these data, it should be kept in mind that the spark source determinations are semiquantitative and that the water-insoluble phases also contain metal oxides and some insoluble sulfates, so the insoluble phase represents more than the glassy portion of the ashes.

No trend is apparent in the data, but this work will be continued on additional coal-fired fly ash samples. It is important to learn about the distribution of these trace quantities of hazardous elements since it appears virtually impossible to pin down their specific compound forms except perhaps by tedious microscopic searches using a STEM instrument to show cation/anion associations.

SUMMARY

Methodology Work

(1) Separations of fly ash samples into water-soluble and insoluble phases simplifies the analytical efforts.

(2) Complete cation-anion determinations are useful in guiding and quantitating the structural analytical techniques.

(3) A new application of infrared spectrometry which uses the capacity and capability of Fourier Transform to store reference compounds and to subtract spectra has been found to offer great potential for the identification of inorganic compounds.

Composition

(1) Oil-fired fly ash emissions are highly water soluble and the water-soluble fractions consist primarily of sulfates. Thus health effects evaluations of the toxicities of metal contents should consider this form in addition to the more commonly tested oxide form.

(2) Coal-fired fly ash emissions also contain a significant water-soluble sulfate phase.

(3) In addition, coal-fired fly ash emissions contain a major glass phase which contains some of the heavy metals deemed hazardous. This glass phase may be less hazardous to health than the water-soluble sulfate phase.

RECOMMENDATIONS

Coal-fired fly ash samples from the Western and Great Plains areas and from petroleum refinery operations should be obtained and analyzed in order to provide a greater representation on which to apply and test the developed methodologies so as to increase the limited analytical data bank on fossil fuel derived particulate emissions.

Consideration should be given to expanding the program scope to examining particulates emitted from nonconventional fossil fuel combustion sources.

A more complete library of reference spectra should be prepared for the Fourier Transform infrared spectrometer work. A planned replacement of the presently used FTS-14, which has limited storage (~20 low resolution files), by an FTS-10 of increased storage capacity will permit permanent cataloging for storage and retrieval of the needed metal sulfate and oxide reference spectra to facilitate identifications in the samples.

Additional studies should be carried out at a microscopic level to examine single particles for compositions as functions of their surface and depth concentrations in order to ascertain the chemical forms of trace constituents in the particulate emissions.

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Investigation of Particulate Sulfur by ESCA

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ABSTRACT

Sulfur species emitted by combustion systems play roles of varying significance in atmospheric chemistry and have been linked to health and ecological hazards. Gaseous and particulate sulfur emissions include a range of oxidized and reduced compounds. We have been investigating particulate sulfur forms emitted by oil-fired and coal-fired combustion sources using X-ray photoelectron spectroscopy (XPS) or ESCA.

In ESCA, a soft X-ray beam strikes a sample, ejecting inner shell electrons from atoms on or near the sample surface. By measuring the kinetic energy spectrum of the photo-ejected electrons, the elemental abundances of particulate surfaces can be determined in concentrations as low as 0.1%. High resolution spectra of individual core electrons reveal a "chemical shift," which is a function of the oxidation state of the precursor element.

As part of this study, a particulate emitted by combustion sources was collected on filters and on impactor substrates. ESCA analyses were performed directly on the filters and substrates with no prior sample preparation. Sulfur species identified include sulfate, sulfite, sulfide, and organic sulfur compounds.

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INTRODUCTION

Environmental effects of inorganic species are functions not only of elemental composition but also of compound form and physical state. A number of analytical techniques are commonly employed to determine elemental composition and anion content of particulate emitted by combustion systems. These techniques include spark source mass spectrometry, X-ray fluorescence, atomic absorption spectroscopy, and wet chemistry. Particulate sulfate is usually determined as the soluble anion by precipitation and turbidity or by acid-base titration.

We report here on an investigation of particulate cations and anions (including sulfates) using X-ray photoelectron spectroscopy, or ESCA, which was undertaken as part of an environmental assessment of the Chemically Active Fluid Bed (CAFB) process. This study, carried out in 1975, was an evaluation of the emissions from the oil-fired CAFB. We are presently engaged in a follow-up program to assess this process for lignite firing.

THE CHEMICALLY ACTIVE FLUID BED (CAFB) PROCESS

The Chemically Active Fluid Bed (CAFB) process was developed by the Esso Research Centre, Abingdon (ERCA), England, as a means to generate electrical energy from high-sulfur, high-metal heavy fuel oil. Fuel oil is fed continuously into a fluidized bed of limestone maintained at 870°C (1600°F) by preheated, substoichiometric air. The fuel oil entering the gasifier is vaporized, oxidized, cracked, and reduced to produce a low-Btu, low-sulfur gas which is then burned in a conventional gas-fired boiler. Sulfur contained in the oil initially forms various gaseous compounds which then react with the bed lime to yield calcium sulfide. The sulfided lime is cycled to a regeneration unit where it is oxidized to produce CaO, which is returned to the gasifier, and SO_2, which is sent to a sulfur recovery unit. An additional feature of the CAFB process is that the gasifier bed material adsorbs vanadium, nickel, and sodium contained in the fuel oil, thus limiting air emissions of these trace elements.

At present, the only existing CAFB unit is a 2.93 MW pilot plant at the ERCA facility. Foster-Wheeler Energy Corporation (FW) is in the final construction stages of a 10 MW retrofit demonstration plant to be constructed in San Benito, Texas, at the La Palma Power Station of the Central Power and Light Company. The ERCA pilot plant is the facility at which all sampling discussed in this paper took place.

SAMPLING

Sampling of the oil-fired CAFB in late 1975 was carried out in accordance with procedures for environmental assessments as they were specified at that time. Particulate sampling was accomplished using a standard RAC train constructed according to the procedures outlined in EPA Method 5. Due to the positions of the installed ports, eight point traverses were taken on two diameters 120° apart. The train was modified slightly to allow for sampling of gaseous organic species. Particulate size distribution measurements were taken with a University of Washington eight-stage in-stack impactor using ungreased substrates. A single point was sampled isokinetically for sufficient time (15 to 30 minutes) to collect a weighable quantity on each stage. In addition to particulate, flue gas was sampled for NO_x by Method 7, SO_2/SO_3 by Method 8, and H_2S by Method 11. An Orsat analyzer was used to measure CO, CO_2, and O_2. In addition to collecting stack-emitted particulate, samples of stack and internal cyclone fines and bed material were acquired.

ANALYSIS

Particulate emissions, cyclone fines, bed material, and fuel were analyzed for trace elements, surface species, and inorganic anions and cations. The principal technique used for elemental determinations was spark source mass spectrometry (SSMS). Atomic absorption spectroscopy (AAS) and wet chemical techniques were employed to supplement the SSMS measurements.

Particulate and solid samples were investigated for surface elements and inorganic compounds using X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA). In ESCA, a high energy X-ray beam (for the analyses reported here, the $MgK\alpha$ line having an energy of 1253.6 eV was used) impinges on a solid, knocking out core electrons from atoms on the solid surface. The resulting electrons pass through an energy analyzer and are pulse-counted by a particle multiplier. The binding energy of the electrons is then calculated from the energy of the incident X-ray, the spectrometer work function, and the measured electron kinetic energy. Binding energy ranges can be uniquely associated with specific precursor elements. In fact, ESCA is sensitive to all elements in the periodic table. An additional feature of ESCA spectra is that the precise electron binding energy in a known range is a function of the valence state of the atom of interest. For example, sulfur combined as sulfate can be differentiated from sulfur as sulfide. In addition, because core electron ejection cross sections are relatively independent of valence state, the ratio of the areas under the peaks corresponding to sulfate and sulfide is a measure of the sulfate-sulfide concentration ratio.

All samples analyzed by ESCA in this study were first scanned over the entire electron binding energy range (broadband scan) to identify those elements present in concentrations greater than 0.1% to 1% (the sensitivity of ESCA to any one element is a function of the photoionization cross section of the most intense core electron emission of that element). These broadband spectra were then analyzed to yield surface concentrations of all identifiable elements. To supplement the bulk SSMS analyses, high energy argon ions were used to etch away surface layers exposing strata 20 to 100 Å deep. The exposed sample layers were then rescanned over the entire binding energy, and the resultant elemental concentrations were compared with the surface and bulk values.

In this study, ESCA was used to analyze impactor substrates, RAC filters, gasifier and regenerator bed solids, and cyclone fines. The principal elements of interest were sulfur and vanadium. The discussion below primarily concentrates on sulfur.

Our interest in examining the particulate and solid matter was to determine the fate of vanadium (550 ppm) and sulfur (3.5%) contained in the fuel oil. The total particulate emission rate for this run was 0.1 lb/10^6 Btu; SO_2 was 1.60 lb/10^6 Btu (828 ppm); and SO_3 was 0.02 lb/10^6 Btu (11.1 ppm). Thus, sulfur emissions were distributed as 98.5% SO_2, 1% as SO_3, and 0.5% as particulate sulfur.

Figure 1 is a broadband ESCA scan of the surface of the stack cyclone particulate. The elements observable on the surface (and thus present at concentrations greater than 0.1%) are oxygen, vanadium, calcium, carbon, sodium, and sulfur. Figure 2 is a scan of the 2p electron of sulfur. Sulfate and sulfide are present at a rate of roughly 3 to 1. Figures 3 and 4 are similar ESCA scans of particulate collected on the RAC filter. Comparison of Figures 1 and 3 indicates that the filter particulate has less surface carbon and more surface sulfur than particulate captured by the cyclone. Figure 4 shows that essentially all particulate sulfur on the RAC filter is sulfate.

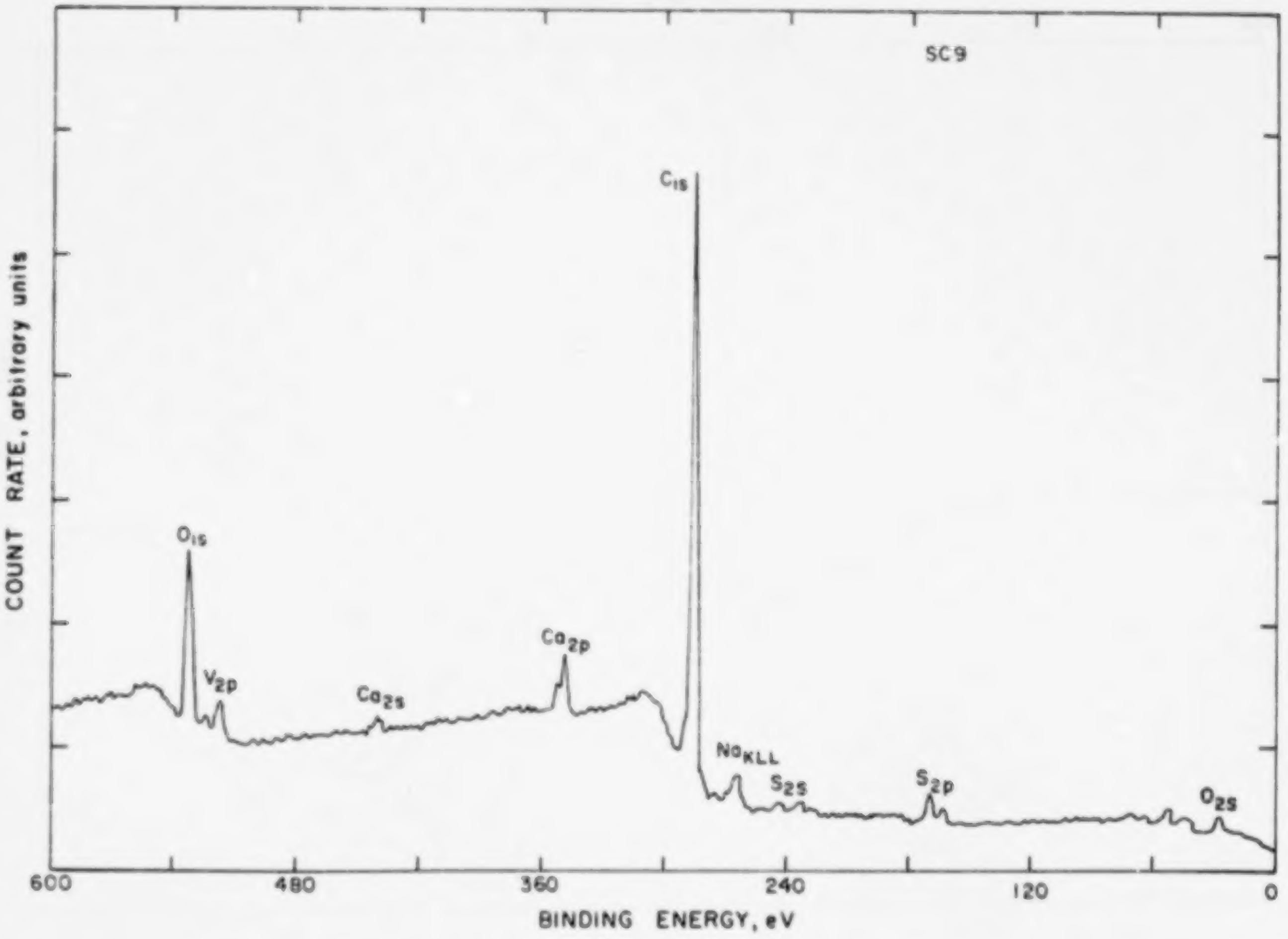

Figure 1. Broadband ESCA scan of stack cyclone particulate.

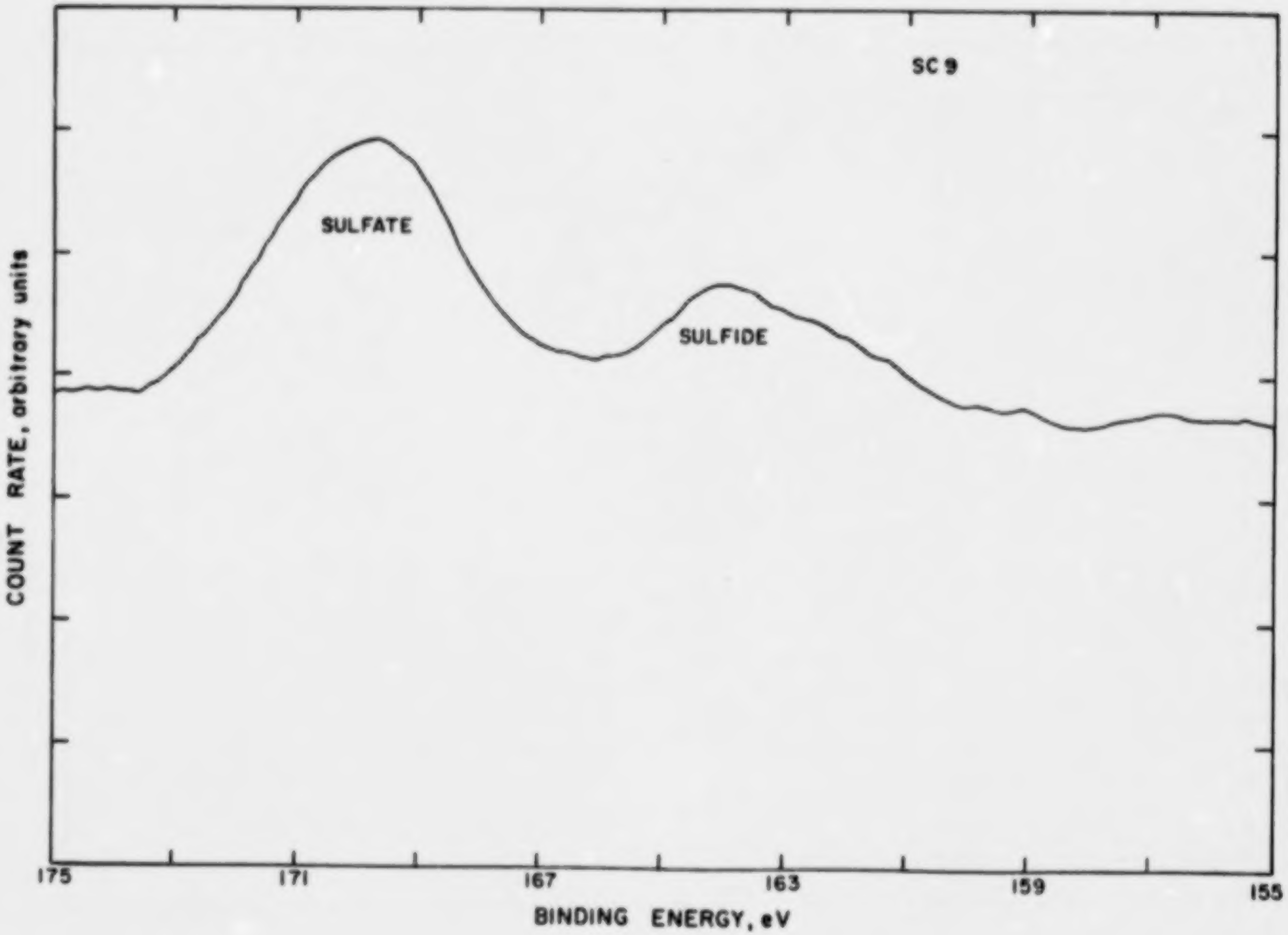

Figure 2. ESCA scan of 2p electron of sulfur of stack cyclone particulate.

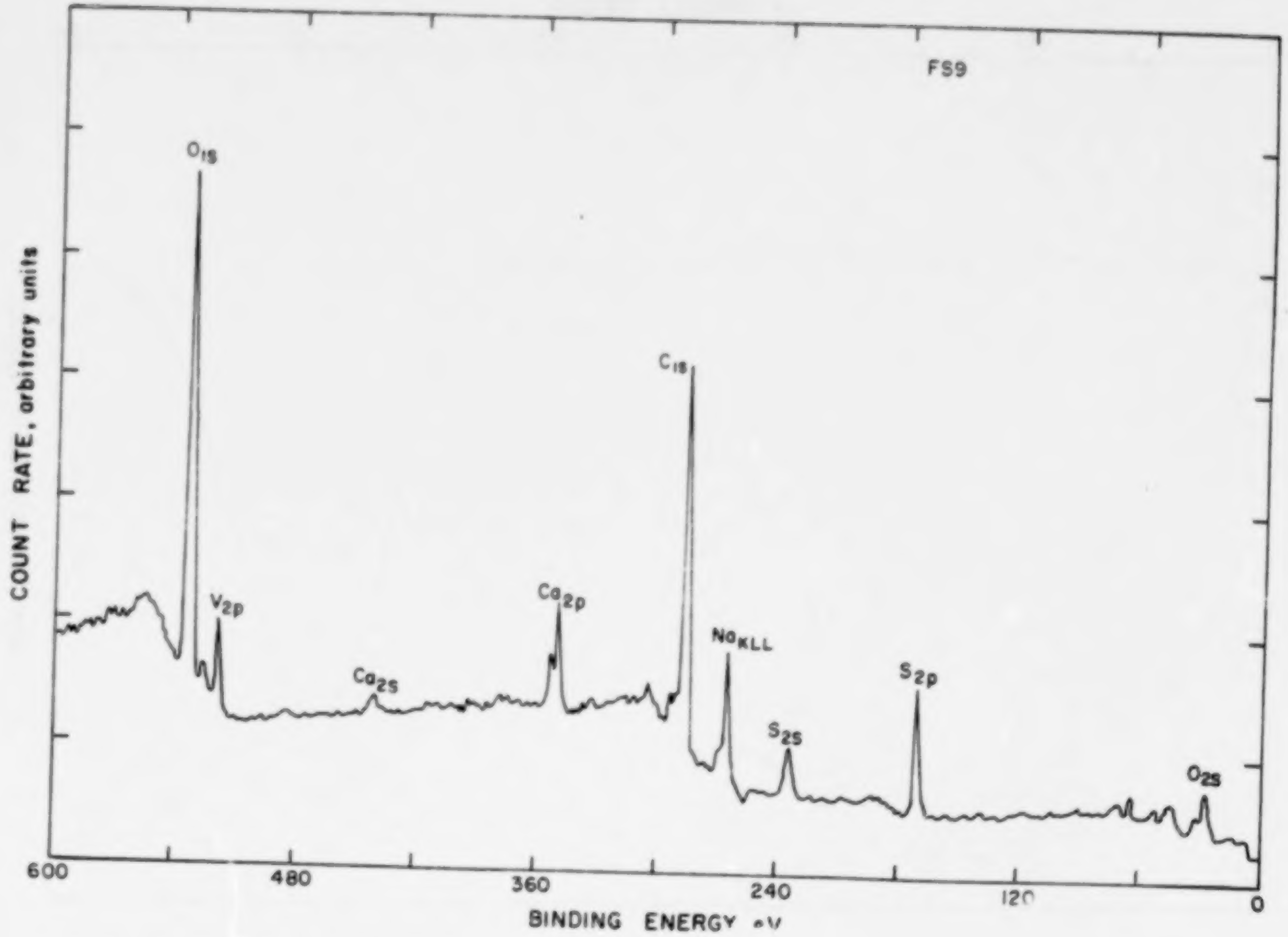

Figure 3. Broadband ESCA scan of sampling train filter particulate.

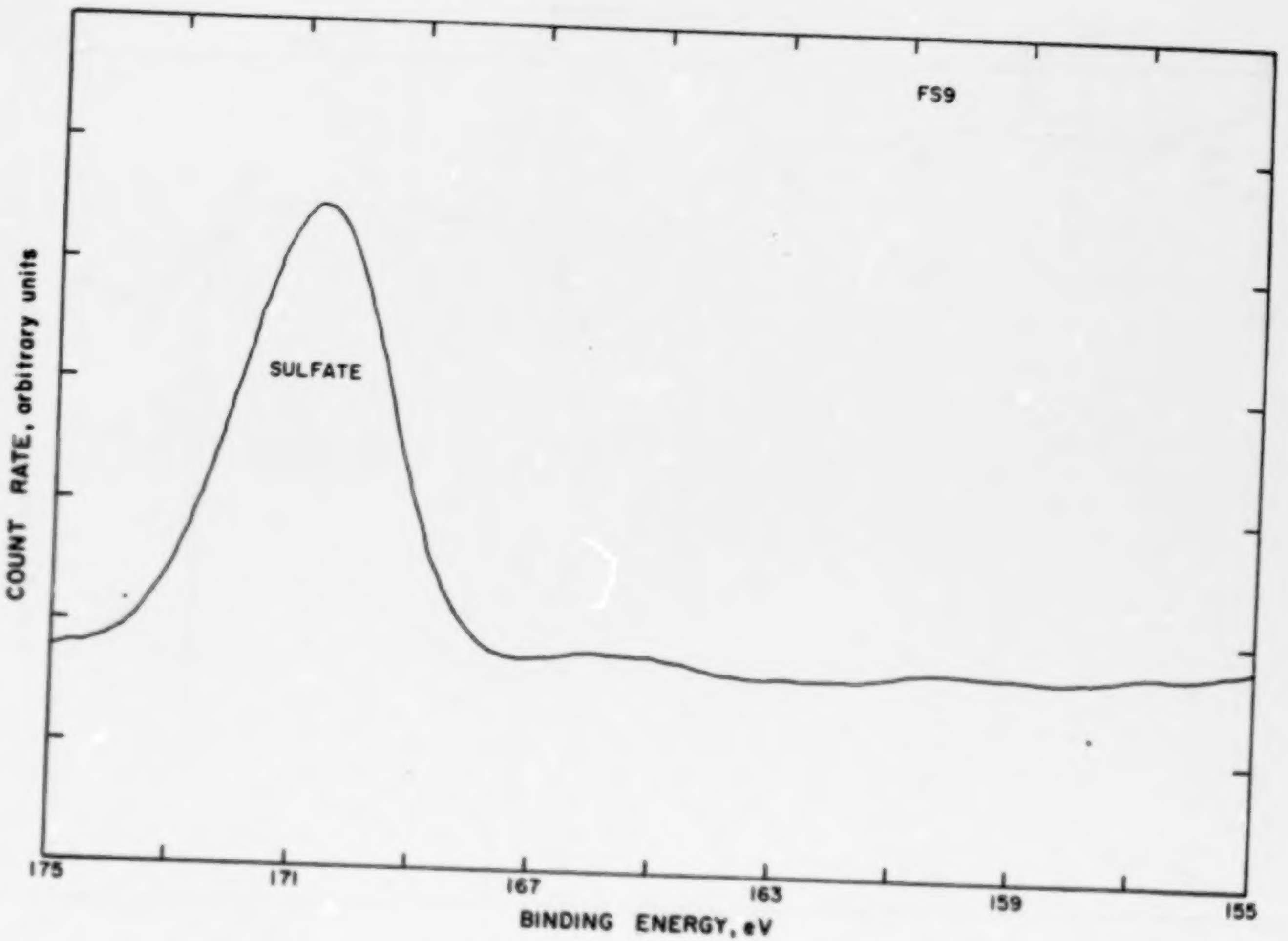

Figure 4. ESCA scan of 2p electron of sulfur of sampling train filter particulate.

To characterize further the compositions of the particulate emissions, each impactor substrate was analyzed by ESCA. Table 1 summarizes the results of broadband scans of each particulate fraction. Fractions are denoted UW91 through UW98 in descending order of size. Columns labeled "surface" refer to scans of unmodified samples; "subsurface" indicates scans taken after etching away roughly 100 Å of surface. Codes SC9 and FS9 refer to stack cyclone and RAC filter particulate, respectively.

It is apparent from Table 1 that the material captured in the stack cyclone is not representative of particulate emissions from the stack. Material captured by the cyclone contains a good deal of unburned carbon and unoxidized sulfur. Most of this material is likely large particulate which passed through the boiler unaffected by the highly oxidizing atmosphere.

The surface/subsurface sulfur ratio of impactor fractions UW91, 93, 95, and 97 indicates that sulfur is clearly enriched on particulate surfaces. This phenomenon is due to two factors: adsorption of sulfur on lime particles in the bed, and condensation and adsorption of gaseous SO_2 and SO_3 on particulate when the flue gas leaves the boiler for the cooler stack region. The latter explanation has been invoked to explain enhanced concentrations of certain trace metals in small ambient particulate. The analogous enrichment on surface versus subsurface of carbon is also partially due to condensation of organics in the stack. However, this should not be overinterpreted because enhanced surface carbon is almost always found by ESCA on samples exposed to ambient air. The surface adsorption explanation is supported by the appearance of calcium in the subsurface scans of impactor particulate but not in the surface scans. The bulk of the particulate is lime from the gasifier bed.

The ongoing lignite study is concentrating on particulate sulfur abundance as a function of depth from the surface. Sulfur to calcium ratios are being measured after etching the surface for various time periods. Preliminary data indicate that sulfur concentrations decrease by a factor of about five from the surface to a depth of 500 Å.

ACKNOWLEDGMENTS

This work was supported by the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, under contract numbers 68-02-1316, task order number 14, and 68-02-2632.

Table 1. Surface and Subsurface Concentrations of Stack Particulate Collected During Oil Gasification

Element	Sample, % abundance														
	SCD	FSD	UW01		UW02	UW03		UW04	UW05		UW06	UW07		UW08	
	Surface	Surface	Surface	Sub-Surface	Surface	Surface	Sub-Surface	Surface	Surface	Sub-Surface	Surface	Surface	Sub-Surface	Surface	Sub-Surface
O	12.8	34.6	34.2	61.0	28.8	37.4	67.9	32.1	34.4	65.9	32.1	30.4	63.8	14.1	10.5
V	1.1	2.4	0.7	1.0	0.4	0.5	0.9	0.6	0.4	0.9	0.4	0.5	1.3	0.3	1.9
N	-	-	2.3	-	2.7	2.3	-	3.1	2.2	-	3.2	2.7	-	-	-
C	80.6	49.8	52.4	31.5	60.7	50.1	28.1	56.2	55.1	29.1	55.6	57.9	30.5	82.4	83.9
Na	0.8	2.9	1.4	0.9	1.0	1.3	0.9	1.5	1.1	0.8	1.6	1.6	1.3	0.8	0.8
S	3.1	7.7	7.9	4.2	6.4	8.3	2.0	6.5	7.0	2.8	7.1	6.9	2.4	2.5	2.8
Ca	1.5	2.6	-	1.4	-	-	1.2	-	-	0.7	-	-	0.7	-	-

See text for explanation of column headings.

Sulfur Emissions Sampling and Analysis

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TRW, DSSG

ABSTRACT

Sampling and analysis for SO_2, H_2SO_4, and particulate sulfate were spurred by the concern over sulfate emissions from flue gas desulfurization (FGD) units.

It has been demonstrated that FGD units remove SO_2; however, it was postulated that they emit potentially more toxic sulfate aerosols. Not enough data are available at the current time to support or reject that supposition.

Over the past three years, TRW has been involved in the sampling and analysis of sulfate particulate and sulfuric acid. This presentation will review the particle size and chemical speciation data collected at several combustion sites employing FGD units.

In particular, this presentation will describe the modifications, the laboratory testing, and the use of the controlled condensation system (CCS) for sulfuric acid collection at combustion sources. Sulfuric acid data collected using the CCS will be presented. The data were gathered during a 60-day test program conducted at the EPA/TVA Shawnee test facility, at a coke oven, and at a full-scale industrial boiler. Sulfate particulate sampling and analysis were undertaken concurrently at the utility boiler. This program included the analysis of particulate matter using XRD, FTIR, and ESCA. The results of these tests will be discussed, and possible analysis approaches will be outlined.

INTRODUCTION

Sampling and analysis for SO_2, H_2SO_4, and particulate sulfate have been spurred by the concern over sulfur oxide emissions from flue gas desulfurization (FGD) units. While it has been demonstrated that the FGD units remove SO_2 efficiently, it has been postulated that they emit potentially more toxic sulfate aerosols.

With this concern over the sulfur oxide output of the FGD, concerted efforts to develop new or improved sampling methods have been conducted by the EPA and its contractors over the last five years. These programs sought to define the problems and improve current sulfate sampling methodology. TRW has been involved in the research and development of methods as well as in the field measurement of sulfates and H_2SO_4 from the outlet of FGD's. This paper will discuss:

- Considerations for sampling oxidizable and volatile sulfur emissions from a wet scrubber, to effectively collect and preserve species.
- The development of H_2SO_4 and sulfate sampling procedures using the controlled condensation system.
- The results of H_2SO_4 and sulfate sampling tests at the EPA/TVA Shawnee FGD test facility and at a coke oven controlled by a charged droplet scrubber using the controlled condensation system.
- Sulfate size distribution at a utility boiler equipped with a soda ash wet scrubber.

SULFITE/SULFATE STABILITY STUDIES

A series of experiments were devised and run to obtain information on the stability of typical sulfate and sulfite compounds which might be expected to be emitted from an FGD. As an initial survey procedure, a Thermal Gravimetric Analysis (TGA) was run. If the TGA results indicated any instability in the 100°-150°C (typical flue gas sampling temperature) range, an isothermal TGA was run which would simulate the thermal conditions that a particle would experience sitting on filter in a standard flue gas particulate matter sampling train. Table 1 summarizes these stability studies.

Table 1. Sulfite/Sulfate Stability Studies

Compound	Thermal Gravimetric Analysis	Isothermal Gravimetric Analysis	Simulated Particulate Sampling
Na_2SO_3	1. Dry Air -No reaction up to 500°C (932°F) -Weight increase of 2% between 500°-625°C (932°-1157°F)		1. 150°C (302°F) - 3 hours with water in the bubbler; 99% of the expected sulfite activity recovered
$NaHSO_3$	1. Dry Air -No reaction up to 150°C (302°F) -Weight loss of 38% between 150°-235°C (302°-455°F)	1. Dry Air - 100°C (212°F) -2% weight loss in a one hour and 20 minute period 2. Dry Air - 150°C (302°F) -38% weight loss in a one hour and 10 minute period 3. Dry Air - 100°C (212°F) -1 part ferrous ferric oxide mixed with $NaHSO_3$. 2% weight loss in a one hour and 20 minute period	1. 150°C (302°F) - 3 hours with water in the impinger; 36% of the expected sulfite activity recovered
Na_2SO_4	Literature reports that Na_2SO_4 is stable up to 1200°C (2192°F). Therefore, it was not tested.		
$NaHSO_4$	1. Dry Air -1% weight loss from 20°-70°C (68°-158°F) -Stable from 70°-170°C (158°-338°F) -14% weight loss from 170°-600°C (338°-1112°F)		
$(NH_4)_2SO_4$	1. Dry N_2 -No weight loss to 225°C (437°F) -Weight loss of 89% from 225°-425°C (437°-797°F)	1. Dry N_2 - 125°C (257°F) -1.8% weight loss in a 3 hour period	
NH_4HSO_4	1. Dry N_2 -15% weight loss from 20°-350°C (68°-662°F) -50% weight loss from 350°-400°C (662°-752°F)	1. Dry N_2 - 125°C (257°F) -1.8% weight loss in a 3 hour period	

In two cases, Na_2SO_3 and $NaHSO_3$, a simulated sampling test was run. This experiment closely approximated the conditions expected in sampling a wet scrubber using the EPA Method 5. A sample train (Figure 1), consisting of an impinger, a tube packed with glass wool, and a 47 mm filter holder, was placed in an oven set at 150°C (302°F). A known weight of powdered Na_2SO_3 or $NaHSO_3$ was placed on a 5.0 μ Mitex Teflon filter and inserted in the filter holder. After allowing the system to equilibrate, laboratory air was bubbled through the impinger with 250 ml of H_2O and was passed through the glass wool and the filter holder. After three hours the filter containing the Na_2SO_3 or $NaHSO_3$ was placed in 10 ml of 0.10 N I_2, which was back titrated with 0.10 N $Na_2S_2O_3$.

The results in Table 1 indicate that at 150°C (302°F) Na_2SO_3 is stable even under conditions stimulating a heated filter in a water-saturated air stream. On the other hand, $NaHSO_3$ decomposes or volatilizes (exhibits weight loss) at 150°C. It is expected that $(NH_4)_2SO_3$ and NH_4HSO_3 will exhibit similar instabilities at even lower temperatures. Ammonium sulfite decomposes at 60°-70°C (140°-158°F) and sublimes at 150°C (302°F), while ammonium bisulfite is delinquescent and sublimes at 150°C (302°F).

In most cases, sampling at an FGD will involve the collection of liquid aerosols possibly containing dissolved scrubber materials. A series of experiments were devised and run to obtain background information on the stability of sulfite compounds under this sampling condition. These experiments were devoted to the study of the stability of sulfite compounds during the collection on a heated filter, where the sulfite aerosol (solution) would be converted to a sulfite particle (solid) on the surface of the filter. As seen above, sulfite compounds have remarkable thermal stability under dry conditions. The objective of the following experiments was to measure the sulfite activity after sulfite solutions were dried. The results of these experiments will provide an indication of the compounds' ability to resist oxidation or decomposition going from a wet to dry state. The procedure employed is described below:

1. Solutions of NH_4HSO_3 and Na_2SO_3 were made up to contain approximately 15-20 $\mu g\ SO_3/10\ \mu l$.
2. A 15 mm (diameter) by 80 mm vial was placed on a hotplate and allowed to thermally equilibrate.

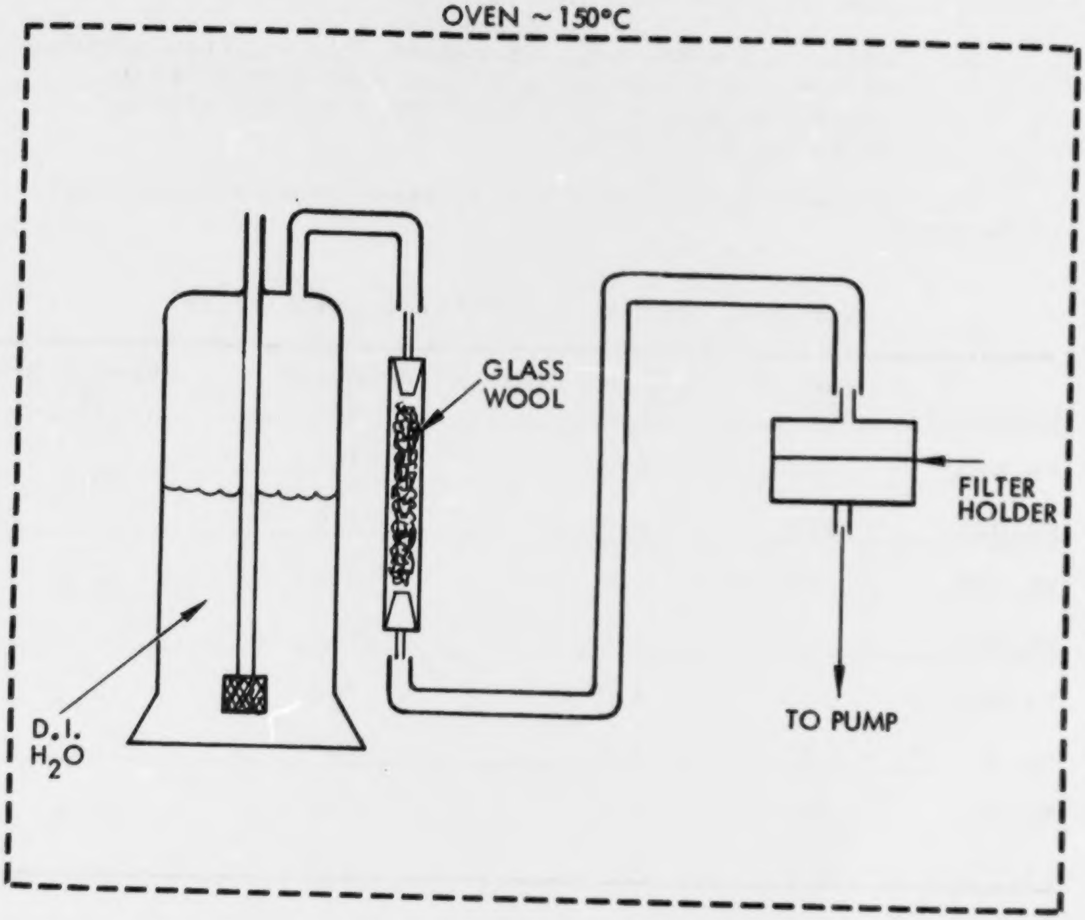
OVEN ~ 150°C
GLASS WOOL
FILTER HOLDER
TO PUMP
D.I. H_2O

Figure 1. Sulfite stability apparatus.

3. Ten µl of each sulfite solution was dropped on the heated bottom of the vial and allowed to dry for a specified amount of time at 125°C (257°F) and at 150°C (302°F).

4. As soon as the liquid was evaporated, 10 ml of 0.1 M tetrachloromercurate (II) (TCM) was added to the vial to stabilize the sulfite.

5. Using the West-Gaeke procedure, the sulfite content in the vials was measured and compared to 10 µl standards placed in a separate vial containing 10 ml of 0.1 M TCM.

The percentage sulfite activity recovered is summarized in Table 2.

Table 2. Wet to Dry Sulfite Stabilities

Compound	Temp. °C	Drying Time (Min.)	Recovery (%)	Average Rec. (%)
NH_4HSO_3	125	4.0	54.2	48.4
NH_4HSO_3	125	4.0	42.6	
NH_4HSO_3	150	1.5	20.0	15.0
NH_4HSO_3	150	1.5	10.0	
Na_2SO_3	125	4.0	4.6	3.3
Na_2SO_3	125	4.0	1.9	
Na_2SO_3	150	1.5	16.3	14.3
Na_2SO_3	150	1.5	12.3	

As can be seen in Table 2, both Na_2SO_3 and NH_4HSO_3 were not stable while being heated to dryness. The relatively high stability of NH_4HSO_3 at 125°C is surprising compared to the low stability of Na_2SO_3 at the same temperature. The higher stability of Na_2SO_3 at 150°C temperature is probably the result of the shorter time (1.5 versus 4.0 minutes) required to evaporate the water; the Na_2SO_3 spent less time in the water being heated, and, consequently, there was less time available for any reaction in the liquid. The same reasoning did not apply to NH_4HSO_3, since by nature it is less thermally stable than Na_2SO_3.

The conclusion resulting from these experiments is that a percentage of the sulfite aerosols sampled on a dry (heated) filter will be oxidized or otherwise changed during the course of sampling a wet scrubber. If sulfite species are to be collected, an approach must be developed that allows for the sulfite species to be collected efficiently under wet conditions and immediately stabilized to ensure that the sample collected reflects the in situ concentration.

SULFURIC ACID/SULFATE SAMPLING PROCEDURES

The systems used to quantify H_2SO_4 are based on selective absorption or controlled condensation. A series of workers (1)(2)(3) have refined the selective IPA absorption method. This approach uses an impinger with 80% isopropyl alcohol to collect the SO_3 and to pass the SO_2. The SO_2 is collected in a back-up impinger of 3% H_2O_2. This method is currently the basis of the EPA compliance test (4) for sulfuric acid mist. The major problem with this procedure is the lack of a pre-filter to effectively prevent particulate matter from reaching the IPA impinger. The particulate matter in the impinger can act either as a direct interferent by contributing $SO_4^=$ from sulfate salts, or as an indirect inferent by catalyzing the $SO_3^=$ to $SO_4^=$ oxidation in the liquid phase through action of trace elements like Fe, Cu, or V.

The controlled condensation approach was first proposed by Knol (5) and has been further developed by Goksoyr and Ross (6). The Goksoyr-Ross system is the basis of an ASTM procedure for SO_x (7). In the controlled condensation approach, SO_3 is separated from the gas stream by cooling the temperature of the flue gas below the dewpoint for SO_3 but above the dew-point of H_2O. The resulting aerosol is either collected on the walls of the cooling coil or on a back-up frit. Investigators (8)(9) studying controlled condensation in the laboratory have found the precision and accuracy to be ± 6% in synthetic gas streams. However, these researchers addressed neither the problem of particulate matter removal nor the possible neutralization of H_2SO_4 by alkaline particulate matter in a filtration system.

A sulfuric acid generator based on the design of Lisle and Sensenbaugh (8) was modified and used to provide test gas streams of varying H_2SO_4, H_2O, SO_2, O_2, and N_2. The generator was a 12 mm O.D. quartz tube with a side arm injection port to introduce liquids onto a heated course quartz frit (Figure 2). The evaporator was wrapped with heating tape to vaporize solutions of H_2SO_4 that were metered into the evaporator using a syringe pump. Gas outlet temperatures ranged from 300°-350°C. Adjusting the H_2SO_4 solution strength and flow produced a range of H_2SO_4 and water concentrations. The rest of the test system (Figure 2) consisted of a heated quartz filter section and a Pyrex Controlled Condensation Coil (CCC). The CCC was a modified Graham Condensor which had a 60 mm medium frit added to one end of the cooling coil.

The preliminary evaluator tests showed that the CCC collected H_2SO_4 efficiently over the ranges of moisture (4%-8%), H_2SO_4 (10 ppm-20 ppm), and CCC temperature (35°-60°C) with a coefficient of variance of ± 7%. Before the system was taken to a coal-fired combustor, an effort was made to determine the effect of fly ash on H_2SO_4 recovery. A series of experiments were run with varying amounts of coal fly ash from TVA Shawnee Power Plant placed on the filter prior to the start of the run. This approach represented a worse case evaluation, since under normal field conditions the H_2SO_4 would see a slowly increasing amount of fly ash. The fly ash was titrated after the run to determine if there was any decrease in the alkalinity of the fly ash. By expressing the decrease in the fly ash alkalinity in milliequivalents, it could be added to the H_2SO_4 recovered from the CCC to determine if an acid mass balance was retained. The results of these experiments are summarized in Table 3.

Table 3. Summary of Fly Ash H_2SO_4 Recovery Tests

Equivalent Fly Ash (g/m^3)	ppm H_2SO_4	% O_2	ppm SO_2	Average Percentage H_2SO_4 Found		
				Filter	CCC	Total
1.3	9	8	0	15	81	96
1.3	12	8	650	14	86	100
1.3	11	8	5300	11	87	98
0.13	11	8	700	0	89	89

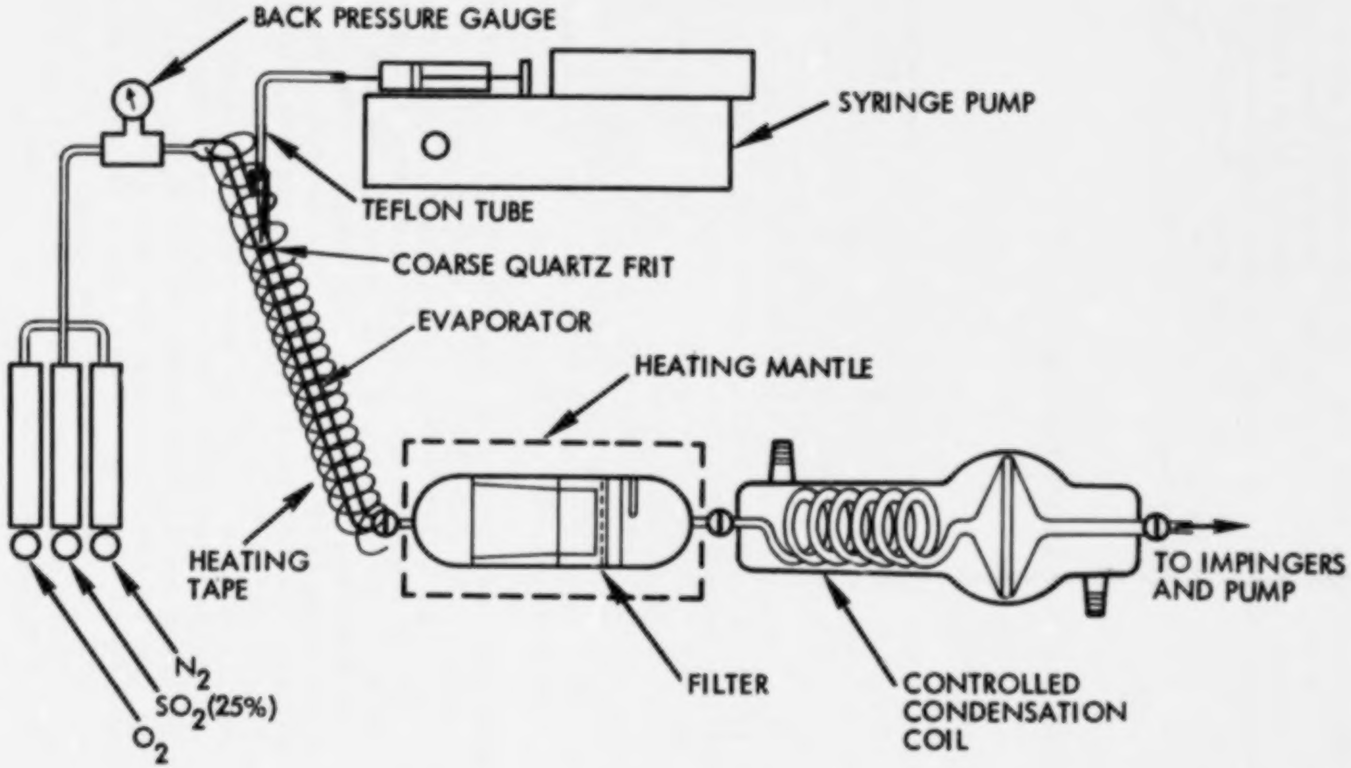
BACK PRESSURE GAUGE
SYRINGE PUMP
TEFLON TUBE
COARSE QUARTZ FRIT
EVAPORATOR
HEATING MANTLE
HEATING TAPE
N_2
SO_2(25%)
O_2
FILTER
CONTROLLED CONDENSATION COIL
TO IMPINGERS AND PUMP

Figure 2. H_2SO_4 test apparatus.

These data indicate that the fly ash reacted with a portion of the H_2SO_4. Within this limited test series, there appears to be a slight improvement in the H_2SO_4 recovery with increasing SO_2 concentrations perhaps because the SO_2 competes with the H_2SO_4 for the alkaline sites on the fly ash. With data available at the present time, it is only possible to estimate that the fly ash caused a 12%-14% reduction in the amount of H_2SO_4 collected by CCC.

SULFATE/SULFURIC ACID FIELD TESTS WITH CCS

Shawnee Test Facility

Extensive field tests with the Controlled Condensation System (CCS) were conducted at a pilot plant located at a TVA coal-fired power plant in Paducah, Kentucky, using the apparatus shown in Figure 3. The H_2SO_4 tests were designed to support an evaluation program of FGD operating parameters being conducted at the Shawnee site. This pilot facility had two prototype FGD units utilizing wet lime or limestone SO_2 scrubbing chemistry. The inlet flue gas mass loadings were approximately 11.4 or 0.17 g/m^3 depending on whether the gas for the prototype FGD's was obtained directly from the boiler or from the outlet of the ESP. Sulfur dioxide concentrations varied from 2,000 ppm to 4,000 ppm at the inlet and from approximately 400 ppm to 800 ppm at the outlet. Gas temperatures and moisture percent varied from 165° to 121°C and 8% to 17%, respectively, across the FGD unit.

Data were obtained from simultaneous inlet/outlet H_2SO_4 measurements across the FGD unit taken over a period of approximately 30 days. The average inlet H_2SO_4 value was 8.3 ppm (ranged from 0.4 to 24.8), while the average outlet value was 3.1 ppm (ranged from 0.0 to 13.9). The average H_2SO_4 removals by the FGD were on the order of 60%, well below the SO_2 removal efficiency seen at Shawnee which typically ranged from 75% to 95%. The fact that the H_2SO_4 removals did not parallel the SO_2 removal indicates that the H_2SO_4 does not exist as a true vapor in the FGD. In fact, under the conditions that exist in the FGD (high humidity and particulate matter for condensation sites), it seems reasonable that SO_3 would exist as a liquid aerosol of H_2SO_4. The size of these aerosols can be inferred from the aerodynamic sizing tests (10)(11) conducted at Shawnee. These tests showed a mass removal by the FGD of ~60% for particles in the range of ~0.5 μ. Further sizing/sulfate analysis studies will be necessary to determine the exact size of H_2SO_4 aerosols.

Since the inlet H_2SO_4 coefficient of variance (CV_T) represents

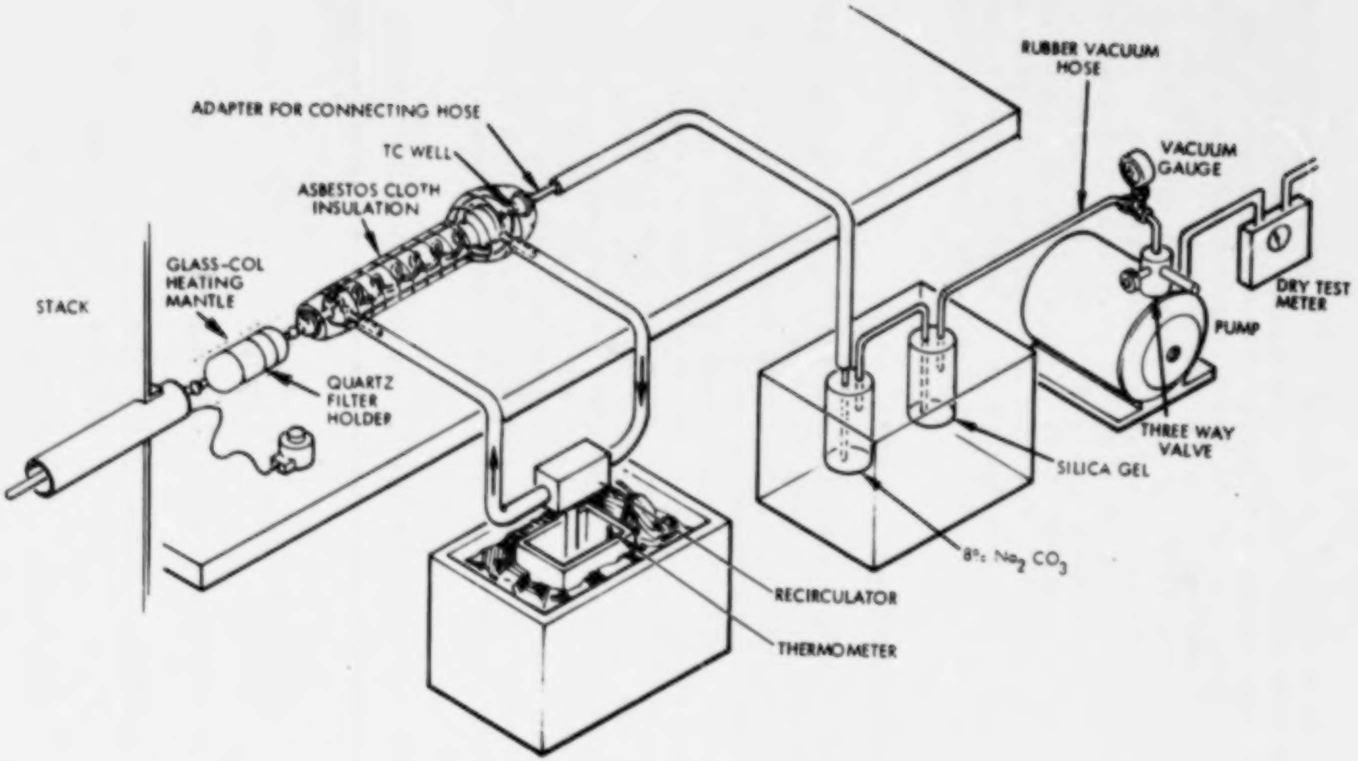
ADAPTER FOR CONNECTING HOSE
TC WELL
ASBESTOS CLOTH INSULATION
GLASS-COL HEATING MANTLE
STACK
QUARTZ FILTER HOLDER
RUBBER VACUUM HOSE
VACUUM GAUGE
DRY TEST METER
PUMP
THREE WAY VALVE
SILICA GEL
8% Na_2CO_3
RECIRCULATOR
THERMOMETER

Figure 3. Controlled condensation system field set-up.

the sum, $(CV_T) = [(CV_S)^2 + (CV_M)^2]^{1/2}$, of source fluctuation (CV_S) and method error (CV_M), the source fluctuation can be estimated by assigning a coefficient of variance to the field CCS. This coefficient of variance reflects errors in reading temperature and pressures, accuracy of leak rates, as well as rinsing recovery or titration errors which might affect the ultimate calculation of the H_2SO_4 concentrations. It is estimated that the field accuracy of the CCS is ± 11%, and thus the coefficient of variance of the source is ± 65%. Samples taken in the morning and evening yield a variance of ± 32.4%. Using these values, Figure 4 was generated. The use of this type of graph will permit the most effective design of a test program to meet accuracy requirements within the time and funding limitations.

Coke Oven Measurements

The same CCS was used to monitor the SO_2/H_2SO_4 content of a waste gas stream from a bank of coke ovens. In this application a three point simultaneous test was performed across a charged droplet scrubber (CDS) used to control coke oven particle emissions. Two separate tests were performed under upset (during coke oven charging, high mass loading) and non-upset (steady state coking period, low mass loading) conditions. The goal of these tests was to determine whether H_2SO_4 was a major contributor to a corrosion problem in the CDS. Consequently, sampling positions were chosen at points where H_2SO_4 could be condensed. Figure 5 shows the gas phase locations: at the inlet, after a pre-quench spray, and after the electrode system (50 feet down-steam). Table 4 contains the results of the tests.

Table 4. SO_2 and H_2SO_4 for Coke Oven/CDS Tests

Condition	Position	SO_2	H_2SO_4 Based on $SO_4^=$	H_2SO_4 Based on H^+
Upset	Inlet	154 ppm	13 ppm	12 ppm
	Pre-cooler	163 ppm	6.4 ppm	17 ppm
	Exit	186 ppm	0	6.4 ppm
Non-upset	Inlet	210 ppm	18.5 ppm	18.2 ppm
	Pre-cooler	199 ppm	13.1 ppm	13.3 ppm
	Exit	217 ppm	5.2 ppm	4.9 ppm

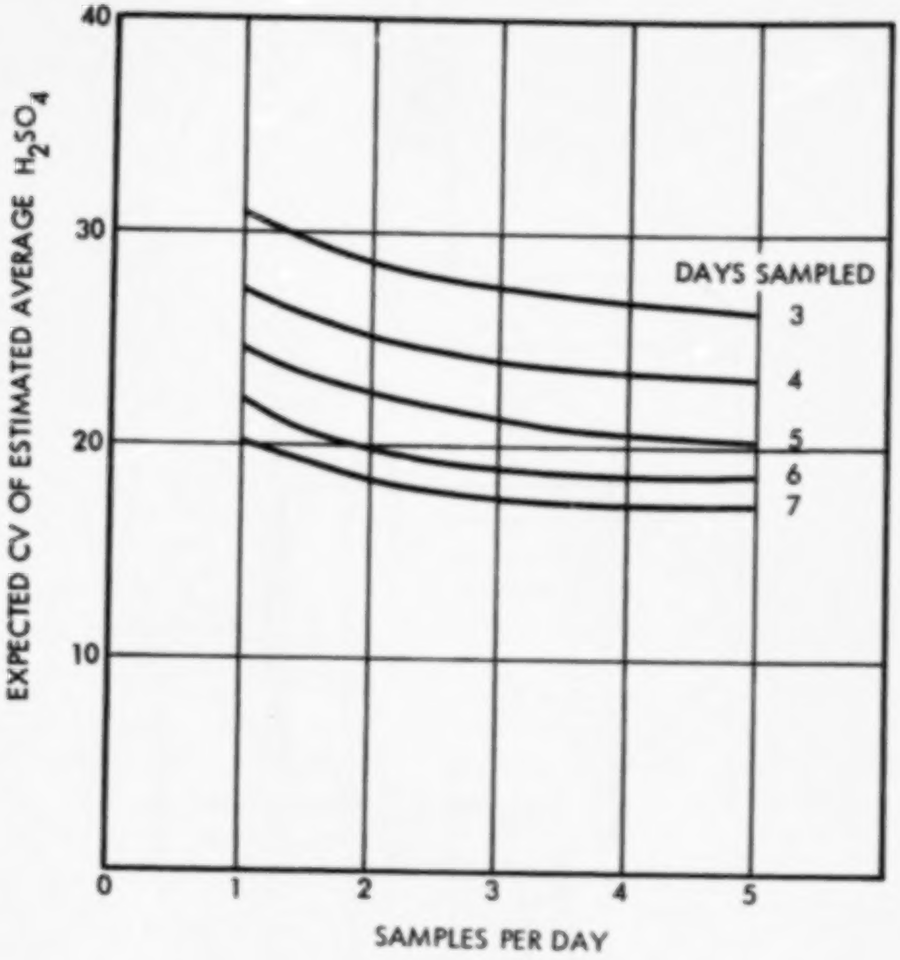

Figure 4. Expected coefficient of variance (CV) of the H_2SO_4 measurement based on the number of samples taken.

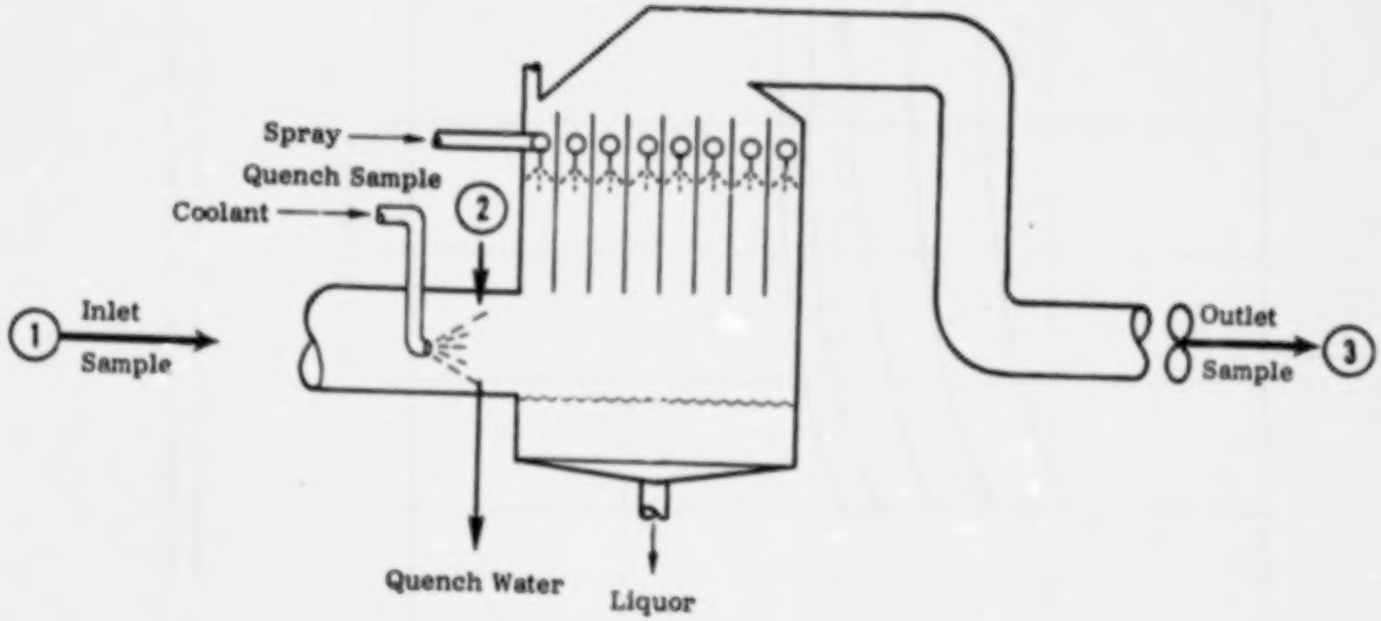
Spray
Quench Sample
Coolant
②
①
Inlet
Sample
Outlet
Sample
③
Quench Water
Liquor

Figure 5. Sampling positions at CDS unit.

In the non-upset condition a steady decline in the H_2SO_4 concentration across the CDS is seen, indicating a removal efficiency of 72% in this low (<10% opacity) mass loading case.

The data for the upset condition are not as clear-cut, since the $SO_4^=$ and H^+ titration of the coil rinse did not agree. It appears that another acidic species was condensed in the coil along with H_2SO_4. Visual observations in the field indicated the coil rinse to be discolored instead of clear as in the non-upset conditions. The plume during the upset condition was black with coal and hydrocarbon aerosol by-products. The filter system, which was heated to 200°C, probably allowed low vapor pressure material to pass to the coil. While there was not enough solution for further confirmatory analysis, it is possible that an organic acid or phenol caused a positive interference with the H^+ analysis.

Using the $SO_4^=$ titration values as the true H_2SO_4 concentration, the CDS was 100% effective in removing H_2SO_4 during the upset condition. The reason for this improved efficiency was probably due to the presence of the large quantity of particles. The H_2SO_4, in the high humidity of the CDS, probably condensed on the solid particles which grew in size because of the hydroscopic nature of sulfuric acid. Once again the H_2SO_4 appears to behave more as a particle than as a gas. In this case, SO_2 (gas) was not removed, while 60%-100% of the H_2SO_4 was removed by the CDS.

SULFATE SIZE DISTRIBUTION TESTS

To gain an insight into the emission of sulfate aerosols from an FGD, TRW conducted an aerosol sizing test at the outlet of a utility boiler controlled with a soda ash FGD. These tests consisted of two runs with a Meteorology Research, Inc. impactor maintained at 121°C. This impactor has seven stages and a filter providing a particle size distribution of ~0.5 to 30 μ. The runs were conducted during times when the boiler was under full and half load, so that a comparison of the size distributions could be made. Figures 6 and 7 show the results of gravimetric and sulfate analysis of each stage.

It is readily apparent that the bulk of the sulfate particles collected were <1 μ. Close inspection of the figures shows that the particle size distribution was skewed to the smaller particles when the boiler was under full load. However, from only these two runs, it is not possible to determine whether boiler combustor

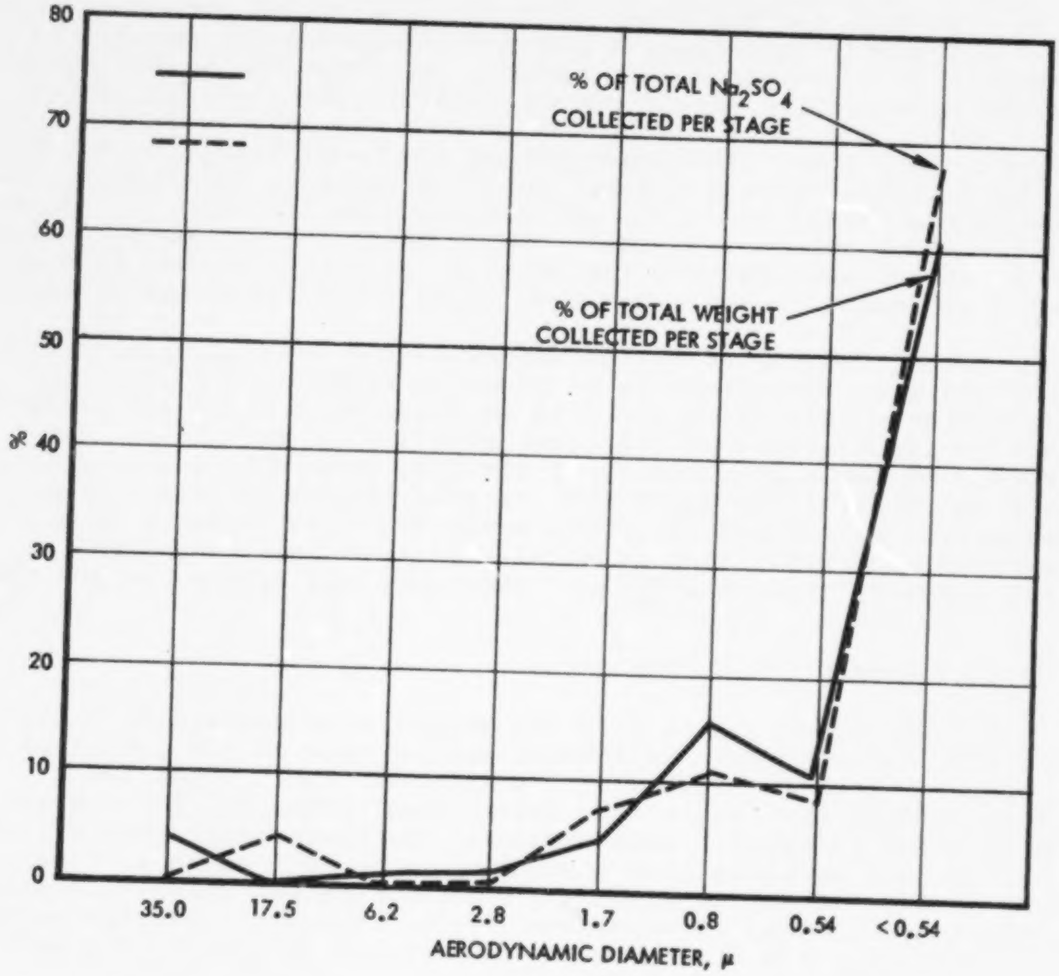

Figure 6. Size distribution of sulfate particles with boiler under full load.

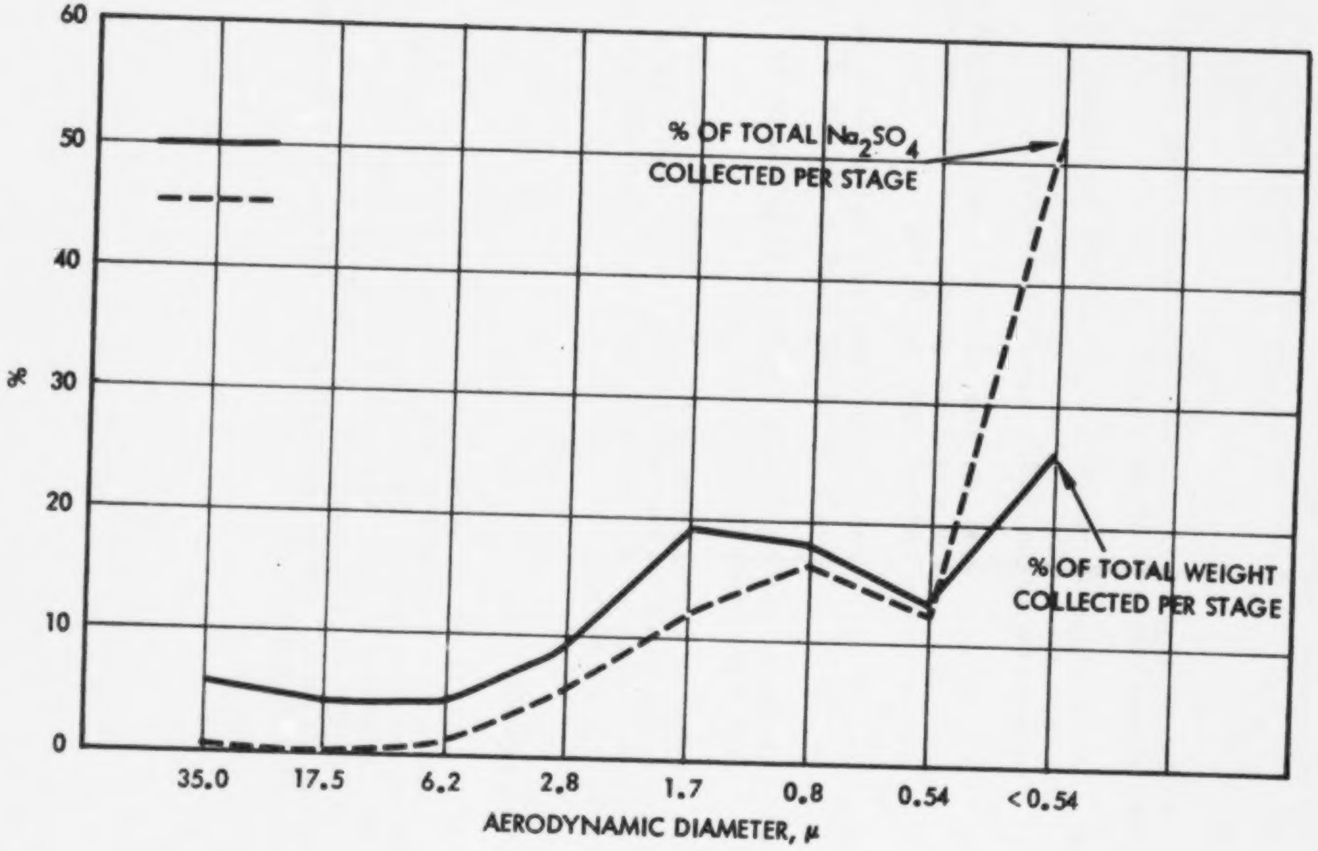

Figure 7. Size distribution of sulfate particles with boiler under half load.

conditions or FGD operating conditions caused the change in the particle size distribution.

SUMMARY

The sampling of sulfate/sulfuric acid from combustion processes poses several problems:

- Stability of bisulfate, sulfite, and bisulfite compounds under conventional sampling approaches is not adequate to maintain their identity.
- Extractive methods for sulfuric acid analysis encounter neutralization problems during the separation of particulate matter and the H_2SO_4.
- Based on removal efficiencies, H_2SO_4 acts more like a small (<0.5 μ) particle than a gas in FGD units.
- Sulfate aerosol size distribution can vary significantly with process conditions.

In order to learn more about the composition of sulfur species, new techniques need to be developed. Only where in situ sulfur species measurements can be made will an accurate picture of sulfur chemistry be attained.

ACKNOWLEDGMENTS

The sulfate/sulfite stability and sulfate aerosol sampling tests were conducted under EPA contract 68-02-21-1412 under the direction of Dr. Robert Statnick. The sulfuric acid sampling studies, Shawnee field tests, and the preparation of this paper were supported by EPA contract 68-02-2165 under the direction of Mr. Frank Briden. Both contracts were from the Process Measurements Branch of IERL/RTP.

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Operating Parameters Affecting Sulfate Emissions from an Oil-Fired Power Unit

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ABSTRACT

Any voluntary or legislated action taken to control sulfates should be based at least in part on a thorough knowledge of the character of primary sulfates (i.e., H_2SO_4 and water-soluble sulfate salts) and on an understanding of the principal variables that govern the magnitude of those emissions.

A system comprising isokinetic flue gas sampling for particulate sulfate on an in situ quartz fiber filter assembly, followed by controlled condensation for H_2SO_4 collection, was used primarily at a high (2.5%) sulfur content oil-fired power unit. Speciation during collection demonstrated that the ESP, depending on efficiency, reduced particulate sulfate generally by 50% to 90%.

Particulate sulfates at a low (0.3%) sulfur content oil-fired unit decreased almost in proportion to the decrease in sulfur content of the oil. Sulfuric acid concentrations were found to correlate well with excess furnace O_2 over the range investigated (0 to ~2% O_2). A good correlation was also found for particulate sulfate and H_2SO_4 at the ESP inlet, with an indication of sulfate formation controlled both in the flame region and in the high temperature heat transfer region. Elemental and carbon analyses indicated that the principal metals in the soluble fraction (Mg and V) nearly accounted for the total measured soluble sulfates. The insoluble fraction was composed primarily of MgO and carbon.

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INTRODUCTION

Any voluntary or legislated action taken to control sulfates should be based, at least in part, on a thorough knowledge of the character of primary sulfates, their emission rates from power plants, institutional and industrial boilers, and apartment and home heating units, and an understanding of the principal variables which govern the magnitude of those emissions. Both for consideration of potential health effects and for determination of the mechanisms and parameters which affect the magnitude and distribution of such emissions, the character of primary sulfates (i.e., H_2SO_4 and water soluble sulfate salts) must be determined with flue gas sampling methods that differentiate between the acid form and the less nocuous sulfates.

A reliable sampling method, utilizing a Brookhaven-designed nozzle and filter assembly (1) for collection, in situ, of flue gas particulates (including water-soluble metal sulfates), followed by a version of the Goksoyr-Ross (2) condenser coil for separate collection of the flue gas sulfuric acid, has been laboratory and field tested at three different power plant units (1)(3). Validation of the methodology has been described (1b) and will be reported in detail elsewhere (4).

The range of emissions of sulfuric acid and particulate metal sulfates at three commercial power plant units will be presented in this paper. The principal plant operating parameters controlling the magnitude of their emission rate, including furnace oxygen, sulfur, and vanadium content of the fuel, and electrostatic precipitator efficiency, have been correlated with emission concentration. Details on the elemental distribution of carbon and the principal metals between the soluble and insoluble particulate fractions will be presented.

With more than one year of sampling experience at the Long Island Lighting Company's (LILCO) Northport Power Station, Unit 3, it was concluded that the full-scale (365 MW) unit, burning fuel oil with an average of 2.4% sulfur and 350 ppm vanadium, was capable of continuous operation with less than 1 ppm of H_2SO_4 and less than 2 ppm of particulate metal sulfates in the flue gas emitted to the stack. Thus, with the proper utilization of furnace and emissions controls, the results in this paper show that even potentially high sulfate emitting oil-fired sources can be readily controlled to less than 0.2% of the sulfur in the fuel emitted as H_2SO_4 and metal sulfates.

EXPERIMENTAL

The Sampling Apparatus

Flue gas sampling was performed primarily with the Brookhaven controlled condensation system (CCS) with some qualified measurements using the Brookhaven version (5) of the Modified (6) EPA Method 6. Basically the CCS (1a) consisted of an in-situ filter for particulates located directly behind the isokinetically sized nozzle, a partially heated glass probe terminating in a 17-turn 6 mm glass coil maintained at 140°F for collection of the H_2SO_4 aerosol, a back-up Pyrex wool plug, a 10-turn coil and receiver vessel maintained at ice water temperature for condensing most of the water vapor, two impingers containing peroxide for collection of SO_2, and finally, a dryer, pump, and dry test meter. A critical orifice and pre-evacuated 1 liter bottle was located between the pump and dry test meter for subsequent chromatographic determination of the flue gas oxygen and carbon monoxide levels at the sampling location.

Analytical Procedures

Specific details on the work-up of the collected material can be found elsewhere (1). The total particulate load on the filter was determined gravimetrically. Then, any free H_2SO_4 was recovered from the filter with a 100% isopropyl alcohol (IPA) wash, and the soluble metal sulfates were recovered with a water wash (5% IPA); negligible sulfur remained on the filter, which was weighed to determine the total mass of the insoluble particulates. The water wash solution was analyzed initially in the program by the Autoanalyzer turbidimetric procedure for total sulfate and later by the more sensitive ion chromatographic approach. A portion of about one-third of the solutions were also analyzed for the principal metals by atomic absorption spectroscopy. The insoluble fraction remaining on the quartz filter was analyzed for carbon and the principal metals by grinding uniformly in a mortar with pestle prior to determination.

The only sulfate fraction to pass the filter, i.e., sulfuric acid, was recovered separately by washing each main section of the sampling system--namely, the probe, the acid condensation coil, and the final filter plug. Generally more than 90% of the H_2SO_4, determined by titration with 0.02 N NaOH with some confirmatory analyses by ion chromatography, was contained on the combination of the probe and the acid condenser coil.

Leaks in the flue ducting were taken into account by comparing the oxygen content at the flue gas sampling location with that in the furnace. The chromatographically determined CO content was used to infer the relative level of furnace oxygen.

Sampling Locations

From November 1976 through March 1978, 81 flue gas sampling runs were performed, 60 of which were performed at LILCO Northport Unit 3. The fuel for the 365 MW oil-fired unit typically contained 2.4% sulfur and 350 ppm of vanadium; the latter was previously shown (7) to be responsible, in part, for the magnitude of the sulfuric acid emissions.

The two sampling locations at Northport Unit 3 were just prior to the electrostatic precipitator (ESP) and just after the induced draft (I.D.) fan on the outlet side of the ESP (Figure 1).

Unit 2 at Northport was essentially the same as Unit 3 with the exception that there was no ESP. (A precipitator is currently being installed, and the unit is projected to be back onstream with the ESP some time after June.) Sampling was performed just at the point where the duct turned into the stack.

The third unit sampled, the Barrett Station Unit 1 at Island Park, New York, was also a tangentially fired boiler, but the fuel was of low sulfur (~0.3% S), low vanadium (~15 ppm V) type. Sampling was also performed at the exit of the induced draft fan. The unit had an ESP, but it was not in operation. The Barrett unit had at one time burned coal but is now exclusively fired with low sulfur oil as mandated by New York City. All three units had Liqui-Mag (MgO) added for corrosion protection.

FLUE GAS SAMPLING RESULTS

Because sampling was performed at three different units, the results will first be presented according to the unit sampled. Subsequently, comparisons will be made of the statistical distribution or range of emissions between each unit.

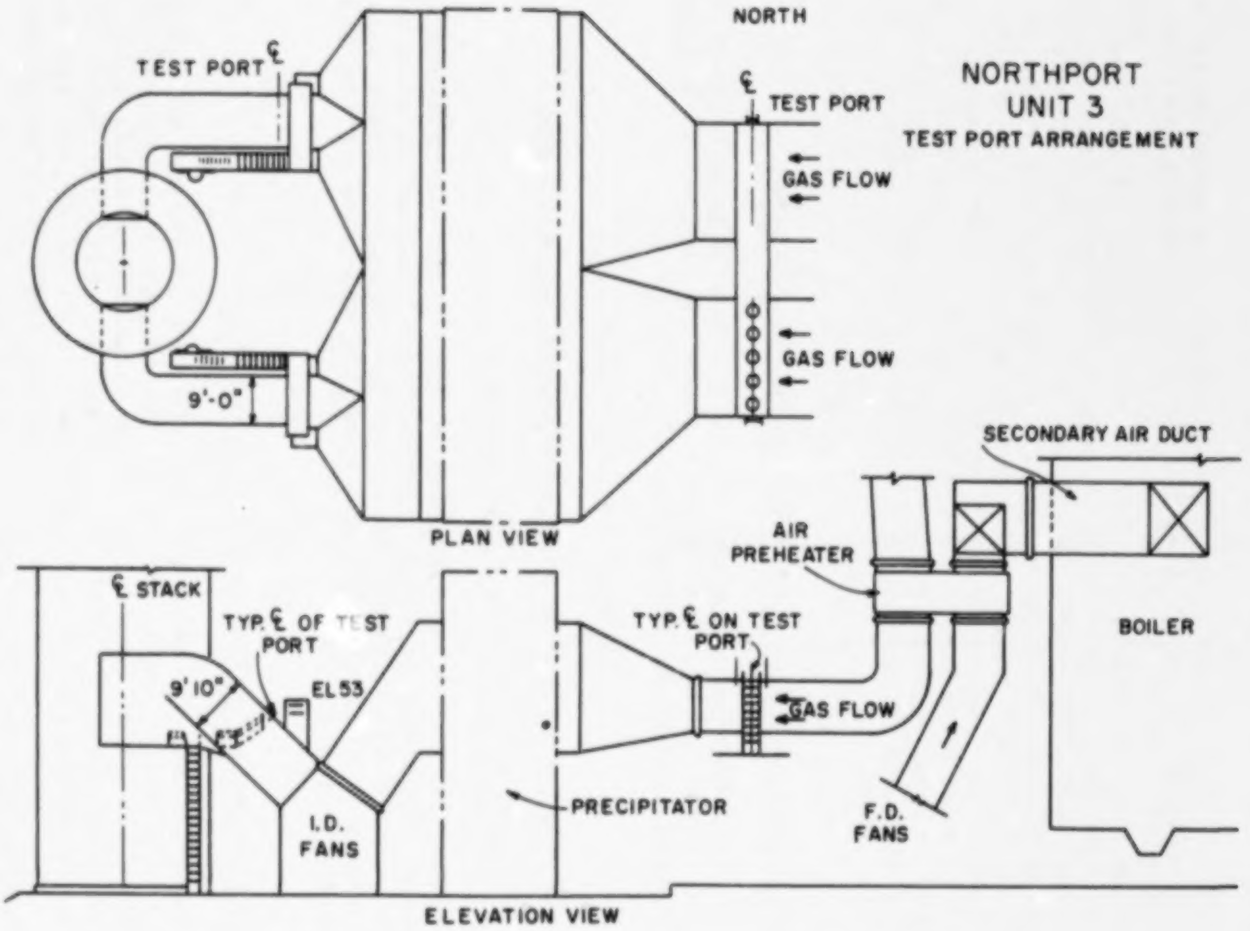
NORTHPORT
UNIT 3
TEST PORT ARRANGEMENT
NORTH
℄ TEST PORT
GAS FLOW
GAS FLOW
TEST PORT ℄
9'-0"
PLAN VIEW
SECONDARY AIR DUCT
AIR PREHEATER
BOILER
TYP. ℄ ON TEST PORT
GAS FLOW
F.D. FANS
PRECIPITATOR
℄ STACK
TYP. ℄ OF TEST PORT
9'10"
EL 53
I.D. FANS
ELEVATION VIEW

Figure 1. Schematic of the sampling port arrangement at Northport Unit 3.

NORTHPORT UNIT 3

The furnace oxygen levels, estimated from consideration of plant measurements as well as the bottle CO levels, varied from 0.0% to 1.1% with an average of 0.25%--indicative of the very close control of combustion air to the stoichiometric requirements. The fuel sulfur level of about 2.4% gave expected SO_2 levels of about 1460 ppm; the measured levels were generally within 3% of the calculated amount. Similarly the measured amount of flue gas water vapor was usually within 5% of the expected amount. The successful attempt at a mass balance for those two compounds placed a certain degree of confidence on the measured levels of sulfuric acid, metal sulfates, and total particulates which, of course, cannot as yet be predicted by any reliable means.

Sulfuric Acid Emissions (Effect of Furnace Oxygen)

Furnace oxygen was shown to play a key role with the level of H_2SO_4 found in the flue gas as shown in Figure 2. A least mean square fit of the data gave

$$[H_2SO_4] = 0.5 + 10.8\,[O_2] \qquad [1]$$

where $[H_2SO_4]$ = sulfuric acid concentration, vol. ppm

$[O_2]$ = furnace oxygen, percent

with a coefficient of determination (i.e., the correlation coefficient, squared) of 0.92, indicating a reasonably good correlation of acid with oxygen level in the furnace. There apparently was no effect whether the sampling was done at the inlet or outlet of the ESP.

Particulate Metal Sulfates (Effect of ESP)

As anticipated, although the ESP had no effect on H_2SO_4, there was a significant effect on the amount of emissions of total particulates, including the water-soluble metal sulfate fraction, as shown in Table 1. In April, with only half the modules in operation at a total power level of 68 KW, the measured total particle removal efficiency was 63% based on the measured outlet and inlet particle level.

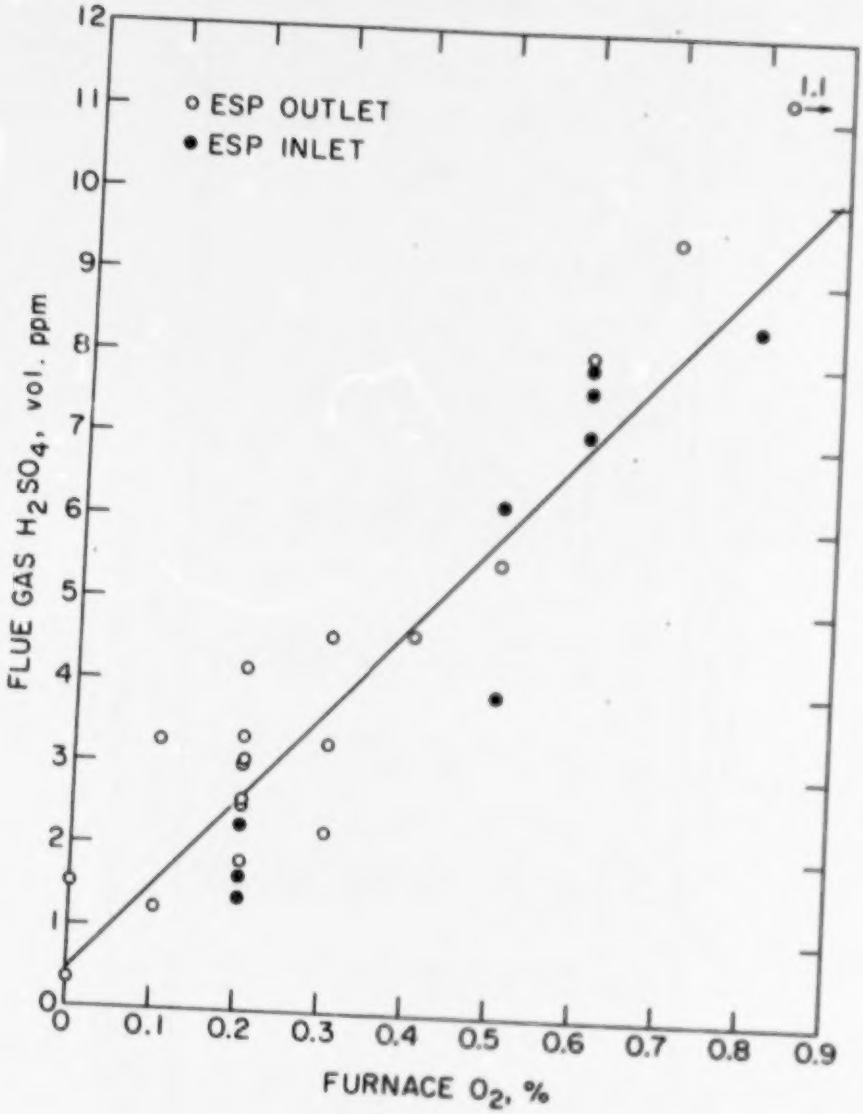

Figure 2. Effect of furnace oxygen on sulfuric acid levels at Northport Unit 3.

Table 1. Effect of Precipitator
(Average Sampling Results at Northport Unit 3)[a]

Date	Location to ESP	Estimated Furnace O_2 %	H_2SO_4 vol. ppm	Soluble Part. $SO_4^=$ vol. ppm	Soluble Part. $SO_4^=$ mg/m^3	Total $SO_4^=$ % of fuel S	Total Part., mg/m^3	Electrostatic Precipitator Efficiency, %	Electrostatic Precipitator Modules on %	Electrostatic Precipitator Operating Power, KW
4/20/77	Inlet	0.6	6.2	15.8	64.0	1.46	157			
4/21/77	Outlet	0.1	1.8	5.2	21.1	0.49	59	63	50	68
5/25/77	Inlet	0.0	<0.02	9.7	39.2	0.66	157			
5/24-AM	Outlet	0.1	1.4	3.1	12.5	0.31	23	86	100	117
5/24-PM	Outlet	0.0	0.3	1.1	4.5	0.10	14	91	100	123
6/24/77	Inlet	0.6	7.0	17.2	69.7	1.67	112			
6/23/77	Outlet	0.8	9.6	1.1	4.6	0.77	6	95	88	118
7/20/77	Inlet	0.2	1.8	12.1	49.1	1.01	140			
7/18/77	Outlet	0.2	3.5	9.2	37.3	0.84	107	28	62	b
7/19/77	Outlet	0.2	3.6	8.8	35.8	0.91	73	51	62	b
10/7/77	Inlet	0.0	0.1	7.0	28.5	0.48	243			
10/4/77	Outlet	0.2	4.5	4.6	18.8	0.62	97	60	62	72
10/5/77	Outlet	0.1	1.4	2.6	10.6	0.25	35	86	75	81
12/14/77	Inlet	0.1	0.3	6.0	24.5	0.42	c			
12/15/77	Inlet	0.3	3.8	13.9	56.3	1.21	c			
12/13/77	Outlet	0.1	0.5	4.1	16.7	0.30	c	--	75	b

[a] Each value is generally the average of 3 or more runs.
[b] Data not available.
[c] Gravimetric particulate weights were inappropriately measured.

In May, about three weeks after the unit had been thoroughly cleaned, all modules were operating at a total power level of 117 KW to 123 KW, and efficiency had increased to 86%-91% removal of total particulate. A month later, even though operating with one module off but at the same total power level, efficiency had climbed to 95%. The higher efficiency, in spite of the lower inlet particulate load which should probably have reduced efficiency somewhat, was probably due to the presence of a larger concentration of H_2SO_4. Experiments have shown that the addition of SO_3 or H_2SO_4 to flue gas streams with normally low acid levels has resulted in improvements in the operation of electrostatic precipitators (8)(9). However, the improved operation of the precipitator with concurrent reduction in sulfate particulate emissions did not off-set the increased emission of H_2SO_4. Thus, total sulfate emissions, i.e., H_2SO_4 plus particulate sulfate, were higher in June.

Only five of the eight precipitator modules were operating during the July runs, total particulate removal efficiency was the lowest of all experiments, and particulate metal sulfate emissions were the highest. In October the ESP was operating only slightly better than in July.

Particulate metal sulfate correlated well with the measured ESP efficiency as shown in Figure 3. From the ordinate on the right it can be seen that the metal sulfate level was reduced to less than 1.5 vol. ppm when the ESP efficiency exceeded about 90%. Thus, with the ESP operating as it was designed, particulate metal sulfate emissions from even a moderately high sulfur-containing fuel can be kept below an emission level of 0.1% of the sulfur in the fuel.

All of the precipitator inlet data from April through July (Data for October and December had not been available yet) were used to plot the ESP inlet particulate metal sulfates versus the measured sulfuric acid level as shown in Figure 4. The slope of nearly unity represented a one-to-one relationship between changes in sulfuric acid levels and corresponding changes in particulate metal sulfates from the boiler. Thus there was apparently a region of the boiler in which the formation of sulfuric acid caused a corresponding increase in metal sulfates. The intercept at 10.2 ppm of metal sulfates at zero concentration of H_2SO_4 implied the existence of another boiler region responsible for the formation of particulate metal sulfates independent of H_2SO_4 levels--i.e., independent of furnace oxygen levels. These observations were only possible because of the utilization of the Brookhaven controlled condensation system which reliably separated the H_2SO_4 from the metal sulfates during the sampling procedure. Further discussion will be given in a later section.

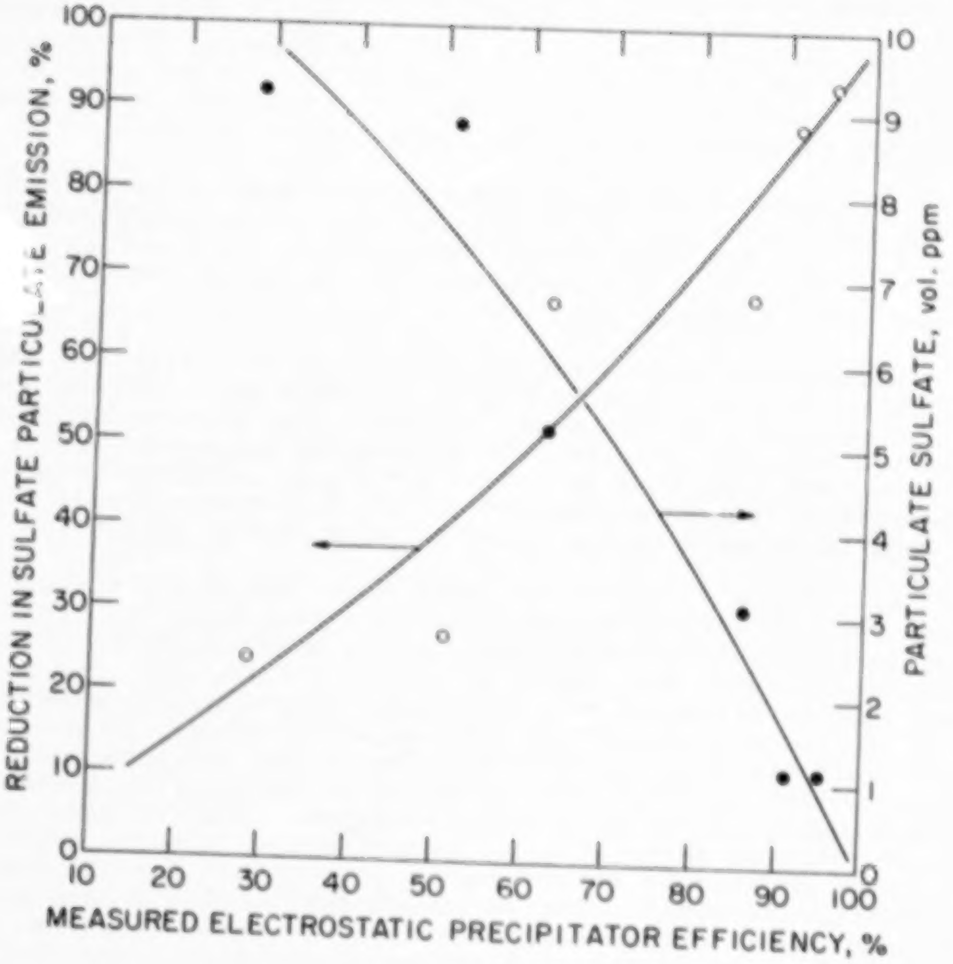

Figure 3. Effect of electrostatic precipitator on the emission of particulate metal sulfates.

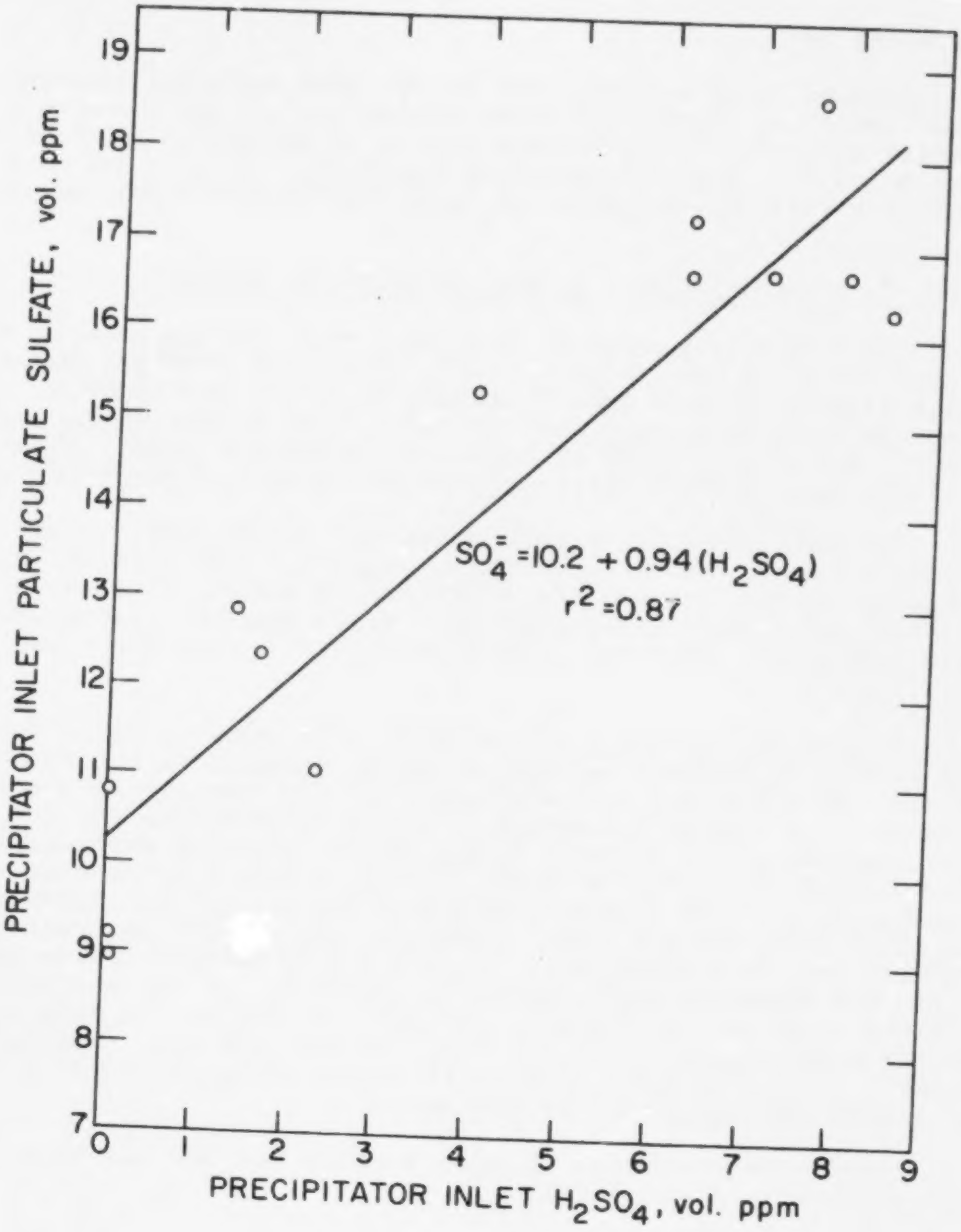

Figure 4. Correlation between particulate metal sulfates and sulfuric acid at the ESP inlet of Northport Unit 3.

NORTHPORT UNIT 2

Because this unit did not as yet have an electrostatic precipitator, which is currently being installed, it was necessary to operate generally with furnace oxygen in excess of 1.5% in order to stay below the opacity emissions standard. As will be seen, this condition resulted in order of magnitude higher H_2SO_4 emissions.

Sulfuric Acid Emissions (Effect of Furnace Oxygen)

Seven sampling runs at this unit were performed with furnace oxygen variable from 1.2% to 2.7%, resulting in H_2SO_4 concentrations ranging from 20 ppm to 40 ppm as shown in Figure 5. Nine sampling runs were performed in April 1978 during which the furnace oxygen varied from 0.4% to 1.0%. Although not shown, those lower sulfuric acid levels indicated the curve went through the origin.

The data for Unit 3 were shown for comparison. There was a higher slope (by about a factor of 1.8) for the data at Unit 2 compared to Unit 3, and the similarities between the units precluded all but one possible explanation. Since the fuel vanadium levels were identical, that key ingredient could not be the answer.

Effect of Fly Ash Recirculation--The most probable cause for the lesser dependence on oxygen may be related to the recirculation of the ESP-collected fly ash back into the furnace in the case of Unit 3. The region suspected of being responsible for the sulfuric acid dependence on furnace oxygen levels was the surfaces of the superheater and reheater tubes in the boiler which became continuously coated with catalytically active (3)(10) vanadium-containing deposits from the oil ash. Based on typical ash determinations, considering that about half the oil ash was deposited as bottom ash (11), and assuming that typically 100 mg/m^3 of fly ash were recirculated back to the furnace, the ash coating on the tube surfaces in the case of recirculation (Unit 3) was probably comprised to a greater extent of less chemically active material than in the case of a once-through (Unit 2) system.

Future measurements at Unit 2 after the ESP has been installed may confirm this hypothesis.

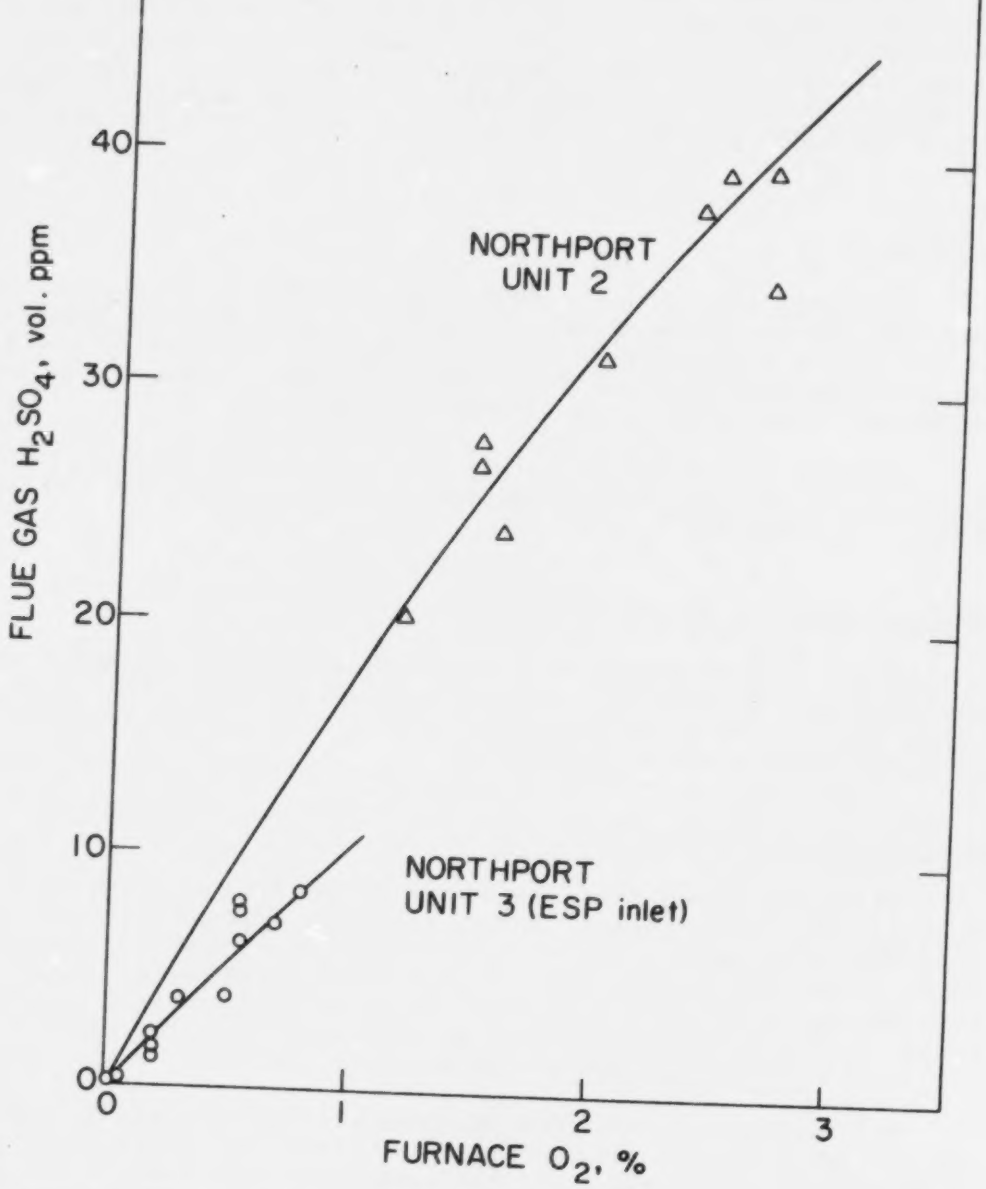

Figure 5. Effect of furnace oxygen on sulfuric acid levels at Northport Unit 2.

Particulate Metal Sulfates (No ESP)

Because there was no electrostatic precipitator and because there was generally an order of magnitude higher H_2SO_4 level in the flue gas of Unit 2 compared to Unit 3, much higher particulate metal sulfates might have been expected. However, the total amount of metals present, including oil ash and MgO additive, limited the metal sulfates to only a 50% increase above that typically at Unit 3.

BARRETT UNIT 1

Although the furnace oxygen levels when sampling at Barrett were generally in the range of 0.5% to 1.0%, the low sulfur content of the fuel, coupled with the low vanadium content of the oil ash, resulted in H_2SO_4 levels less than 0.2 ppm. Particulate metal sulfates ranged from about 2 ppm to 4 ppm.

Because the levels were of such a reduced magnitude compared to those at Northport, it was not possible to deduce the effect of furnace oxygen.

OVERALL RESULTS AT ALL UNITS

Since a large number of measurements had been made, an easier way to view the general range of emissions from each of the three units was in the form of histograms or frequency-distribution diagrams as shown in Figures 6 through 9.

Northport Unit 3 Distribution

Figure 6 shows that the range of sulfuric acid flue gas concentrations at Northport Unit 3 was from 1 ppm to 11 ppm at the electrostatic precipitator outlet and from 1 ppm to 9 ppm at the ESP inlet, that is, independent of the ESP. Similarly, the average at the outlet (3.3 ± 2.6 ppm) was essentially identical to that at the inlet (3.2 ± 2.8 ppm). Thus, as expected, the ESP had no effect on the flue gas vapor phase sulfuric acid content.

On the other hand, the particulate metal sulfate did reflect the presence of the precipitator. At the ESP inlet (lower histogram in Figure 7), the range of metal sulfates was from 5 ppm to 19 ppm with an average of 11.9 ± 4.2 ppm. At the outlet (upper histogram),

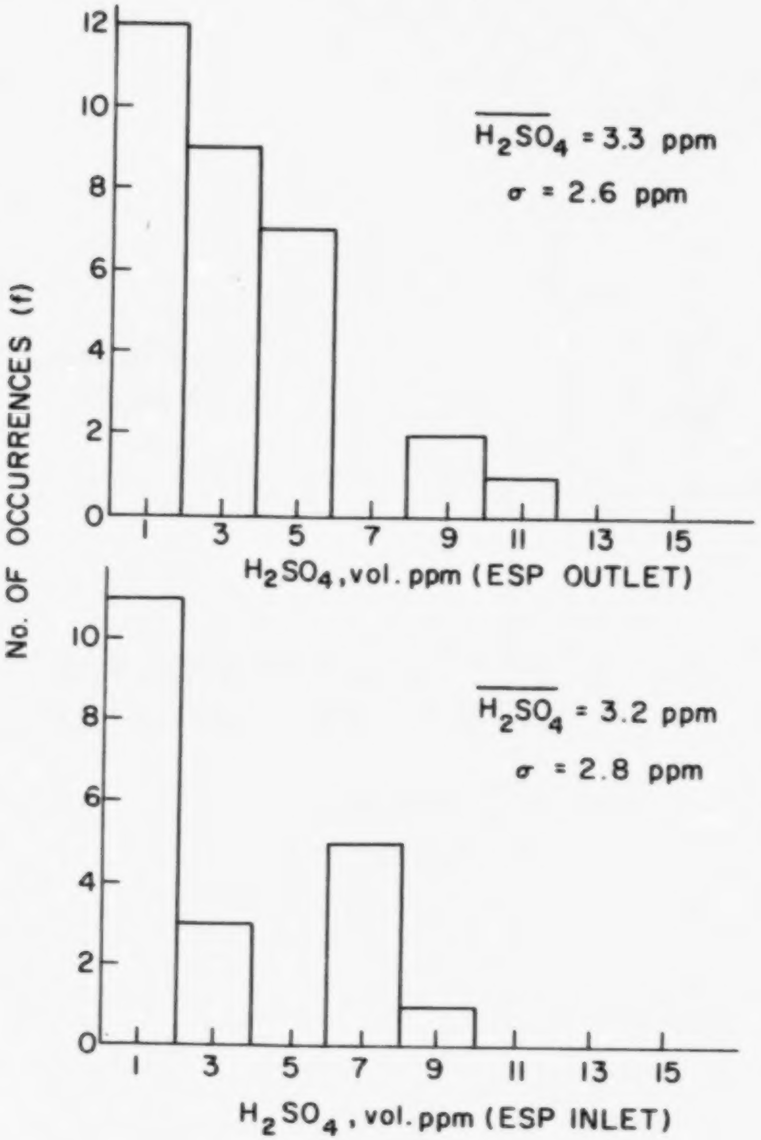

Figure 6. Histograms of sulfuric acid emissions at Northport Unit 3: (upper) at the ESP outlet; (lower) at the ESP inlet.

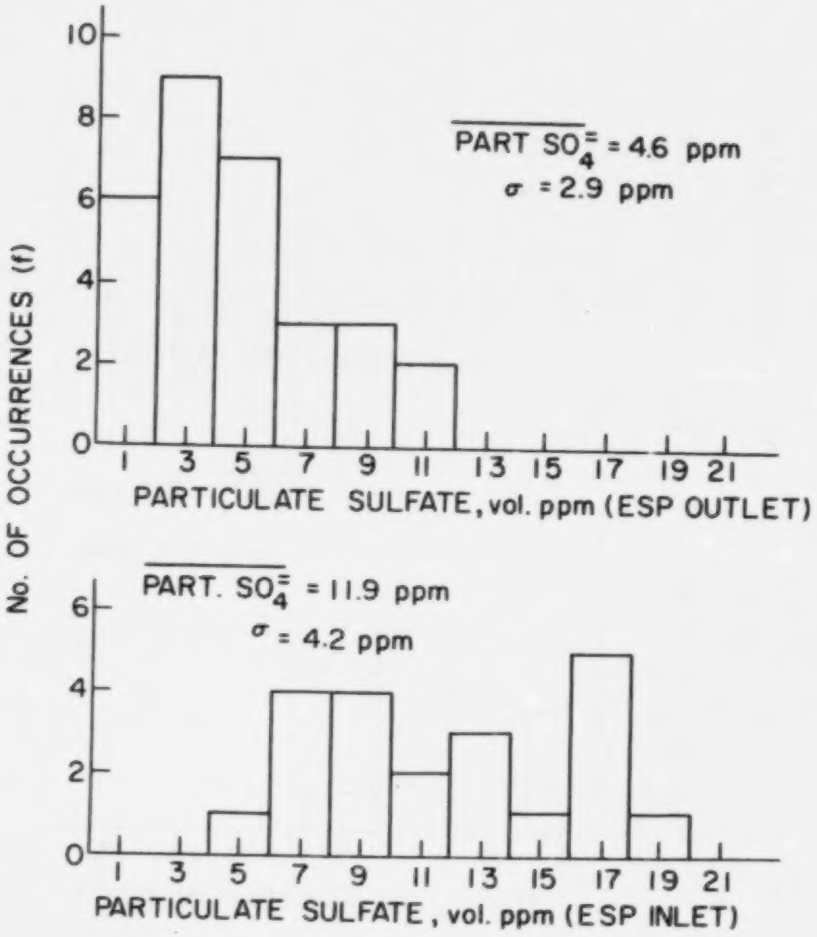

Figure 7. Histograms of particulate metal sulfates at Northport Unit 3: (upper) at the ESP outlet; (lower) at the ESP inlet.

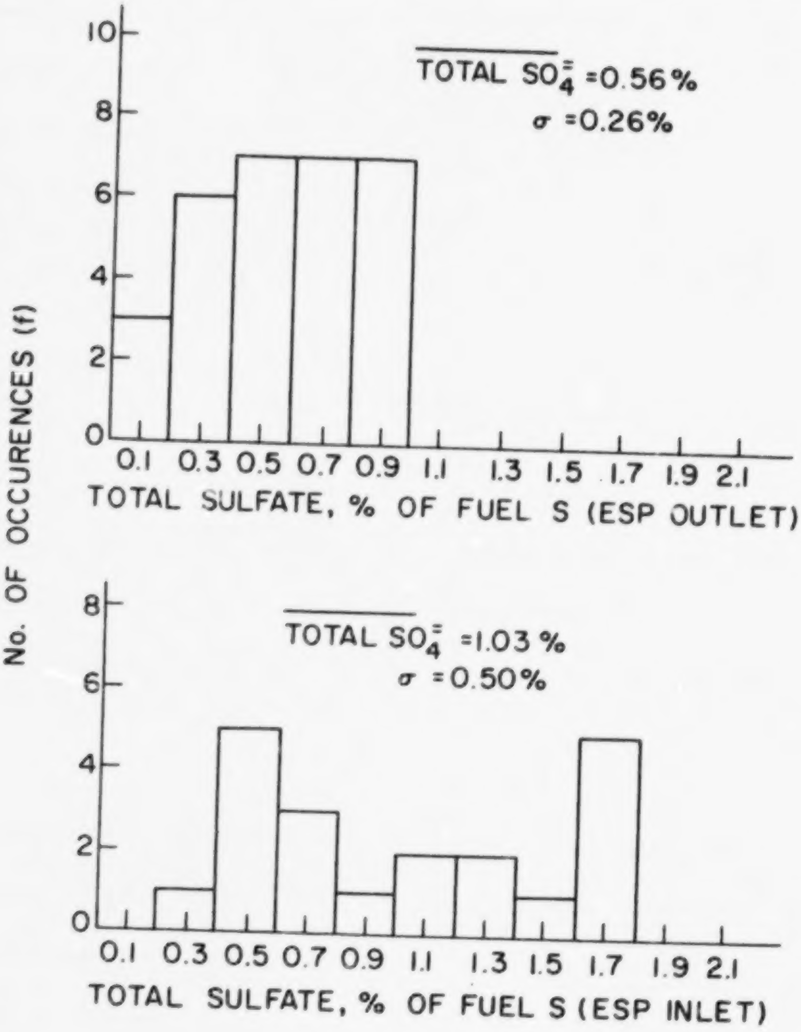

Figure 8. Histograms of total sulfate emissions at Northport Unit 3: (upper) at the ESP outlet; (lower) at the ESP inlet.

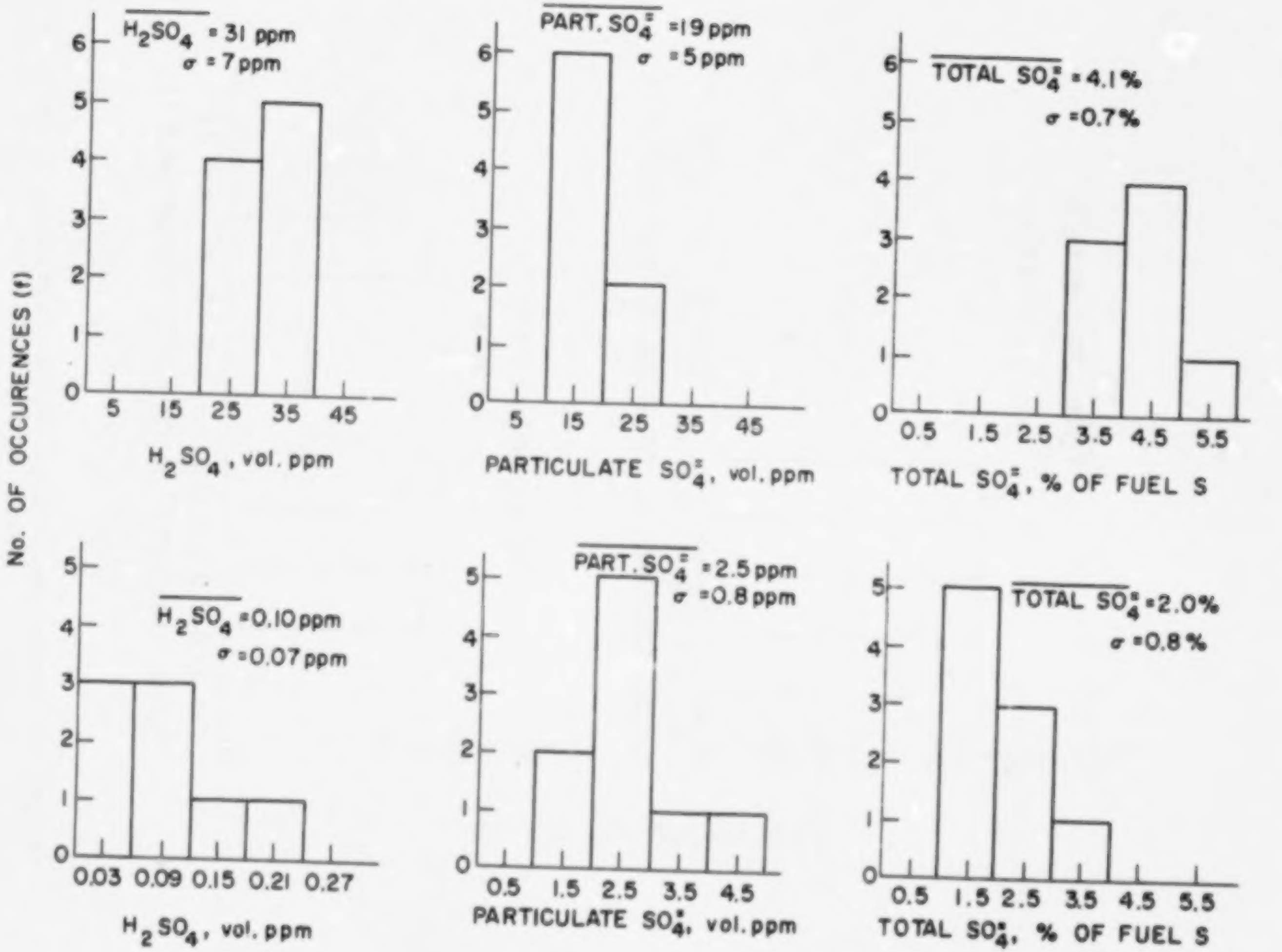

Figure 9. Histograms of sulfur emissions at two oil-fired units: (upper) Northport Unit 2; (lower) Barrett Unit 1.

the range was less--from 1 ppm to 11 ppm--as was the average, 4.6 ± 2.9 ppm. Thus, on the average, the ESP reduced metal sulfates by 61%.

Total sulfates, i.e., the sum of the H_2SO_4 and the metal sulfates, expressed as a percentage of the sulfur in the fuel, are plotted in Figure 8. At the ESP inlet (lower curve), the range was much broader than at the ESP outlet. On the average, the total sulfate emissions to the stack were 0.56 ± 0.26% of the sulfur in the fuel.

Northport Unit 2 Distribution

The upper portion of Figure 9 shows the histograms for the concentrations of H_2SO_4 and metal sulfates in the flue gas at Northport Unit 2 as well as the total sulfate emissions as a percentage of the fuel sulfur. Comparing the average H_2SO_4 emissions at Unit 2 (31 ± 7 ppm) with those at Unit 3 (3.3 ± 2.6 ppm), nearly an order of magnitude higher acid emission was present at Unit 2. The metal sulfate concentration (19 ± 5 ppm) was only about 50% higher than that at the ESP inlet of Unit 3 but 4 times higher than the metal sulfate entering the stack at Unit 3.

Role of the Northport ESP--Both the much higher acid levels and the somewhat higher metal sulfate levels at Unit 2 compared to Unit 3 indicated that the ESP played a very important role--a somewhat direct role with respect to the metal sulfate emissions and an indirect role with respect to the acid. Burning the fuel oil at a furnace oxygen level of 0.2 ± 0.3%, as was the case for Unit 3, resulted in a very heavy soot load when nearly the same oxygen level was used at Unit 2 (April 1978 tests not yet available). The resulting black plume, which was at the threshold of opacity emission standards, was not especially aesthetically appealing. In order to reduce the visibly dark plume, the unit without the precipitator normally resorted to combustion at the moderate level of furnace oxygen of about 1.0% to 1.5% O_2. Thus the amount of oxygen available for increasing the rate of catalytic formation of H_2SO_4 was generally from 4 to 6 times higher at the uncontrolled unit compared to that with the ESP. In addition, recirculating the fly ash removed by the ESP back into the furnace apparently reduced the overall catalytic activity of the surfaces by about a factor of two.

Thus, the ESP allowed the emissions of total sulfate, on the average, to be reduced from 4.1% to 0.56% of the sulfur in the fuel--a 7-fold reduction.

Barrett Unit 1 Distribution

The sulfuric acid emissions at Barrett, as shown in the lower portion of Figure 8, were remarkably lower than those at Northport Unit 2--0.10 ± 0.07 ppm compared with 31 ± 7 ppm, respectively--that is, over 300-fold lower. Yet, the particulate metal sulfates were only about 7 1/2-fold lower (2.5 ± 0.8 ppm) than at Unit 2 (19 ± 5 ppm).

Role of Fuel Sulfur and Vanadium--Assuming that flue gas sulfuric acid was primarily controlled by and directly dependent on the sulfur content of the fuel, the vanadium content of the fuel, and the furnace oxygen level, then the ratio of the product of those three variables to the average H_2SO_4 concentration should be about the same for each unit. As shown in Table 2, the aforementioned ratios were, indeed, very nearly identical, giving strong weight to the direct dependence of H_2SO_4 on sulfur and vanadium content.

Table 2. Effect of Fuel Sulfur and Vanadium

Unit	Average Fuel Oil Content		Average O_2, %	Product[a]	Average H_2SO_4, ppm	Ratio of Product to H_2SO_4
	Sulfur, %	Vanadium, ppm				
Northport Unit 2	2.1	390	2.0	1638	31	53
Barrett Unit 1	0.3	15	1.0	4.5	0.10	45

[a] Product of sulfur content times vanadium content times furnace oxygen.

Future studies should be conducted at one unit for which the sulfur, vanadium, and furnace oxygen could be varied in a systematic fashion.

ANALYSIS OF COLLECTED PARTICULATES

To obtain a better understanding of the mechanisms and variables affecting the emissions of H_2SO_4 and particulate metal sulfate, a selected number of the water wash solutions from the nozzle filters, as well as the remaining particulates on the filter, were analyzed for the principal metal content. Material balances based on the stoichiometry for the metal sulfates and oxides were performed, and the information was used to do a metals inventory on the power plant. Examples of those results are shown in the following section. Complete details are available in other reports (1a)(3a).

Particulate Material Balances (Water Soluble)

Determinations of some of the water washings containing dissolved metal sulfates were made for the principal metals--typically Mg, V, and Na with smaller amounts of Ni and Ca and traces of iron--as shown in Table 3. Assuming that the stoichiometric amount of sulfate with each element corresponded to that for the compounds shown in the table, the sum of those amounts was shown to differ from the total sulfate measurement by generally no more than ± 10%.

By summing the individual compound concentrations, comparison was also made with the total water-soluble particulate concentration determined by difference between gravimetrically determined total particulate and insoluble particulate. The agreement in the last two columns was very good.

The choice of compound formulations for each of the sulfate salts was unambiguous except for nickel and iron--the lower (-ous) valencies were assumed. For vanadium, the principal sulfate has been shown to be vanadyl sulfate, $VOSO_4$ (12). The hydrate formulations were assumed to be the highest hydrate stable at the conditioning humidity of the filter assemblies using data available in the literature (13)(14). The hydrates of $MgSO_4$ were the most stable with the presence of $MgSO_4 \cdot 6H_2O$ having been demonstrated by other workers using X-ray diffraction (15).

Particulate Material Balances (Water Insoluble)

As shown in Table 4, the principal insoluble metals also involved Mg and V with smaller amounts of Ni and Fe and traces of Na and Ca. However, carbon contributed substantially to the insoluble fraction, generally the largest of any element present. The sum of the stoichiometrically determined metal oxides plus carbon differed from the gravimetrically determined total insoluble particulate by generally less than ± 30%; the sum was probably the more accurate number.

Table 3. Detailed Analyses of Soluble Particulates[a]

Run[b]	Flue Gas, m^3	Mg (SO_4)[c] $[MgSO_4]$[d]	V (SO_4) $[VOSO_4]$	Na (SO_4) $[Na_2SO_4]$	Ni (SO_4) $[NiSO_4]$	Fe (SO_4) $[FeSO_4]$	Ca (SO_4) $[CaSO_4]$	Total Sulfate		Total Soluble	
								Σ[e]	Meas.[f]	Σ[g]	Meas.[h]
PR-31-0	0.3484	4.74 (18.7) [37.5]	1.02 (1.9) [3.3]	2.38 (5.0) [7.4]	0.52 (0.9) [1.4]	0.04 (0.1) [0.2]	0.86 (2.1) [2.9]	(28.7)	(32.0)	[52.7]	[53.5]
34-0	0.2920	4.85 [19.2] [38.4]	2.10 (4.0) [6.7]	3.23 (6.8) [10.0]	0.53 (0.9) [1.4]	0.02 (0.1) [0.1]	1.11 (2.7) [3.8]	(33.7)	(35.7)	[60.4]	[62.1]
36-0	0.2973	4.49 (17.8) [35.5]	3.53 (6.7) [11.3]	2.64 (5.5) [8.2]	1.13 (1.8) [3.0]	0.04 (0.1) [0.2]	- - -	(31.9)	(30.0)	[58.2]	[56.2]
27-I	0.2246	7.06 (27.9) [55.8]	5.12 (9.7) [16.4]	3.74 (7.8) [11.6]	0.85 (1.4) [2.2]	0.03 (0.1) [0.1]	- - -	(46.9)	(45.0)	[86.1]	[73.8]

[a] All concentrations in mg/m^3 of flue gas determined from elemental atomic adsorption
[b] O after run no. represents sampling performed at Northport electrostatic precipitator outlet; I, inlet
[c] Calculated stoichiometric amount of sulfate
[d] Calculated as $MgSO_4 \cdot 4H_2O$; all other sulfate salts were anhydrous at desiccator humidity
[e] Sum of the stoichiometric sulfates
[f] From ion chromatograph total soluble sulfate determinations
[g] Sum of the stoichiometric metal sulfate salts
[h] Difference between gravimetrically determined total particulate and insoluble particulate

Table 4. Detailed Analyses of Insoluble Particulates[a]

Run[b]	Flue Gas, m^3	Mg (MgO)[c]	V (VO_2)	Na (?)	Ni (NiO)	Fe (Fe_2O_3)	Ca (CaO_2)	Carbon	Total Insoluble	
									Σ[d]	Meas.[e]
PR-31-0	.0.3484	4.84 (8.0)	5.10 (8.3)	- -	0.36 (0.5)	4.93 (7.0)	0.19 (0.3)	(22.5)	(46)	(68)
34-0	0.2929	3.65 (6.0)	4.73 (7.7)	- -	0.39 (0.5)	4.14 (5.9)	0.15 (0.3)	(12.5)	(33)	(41)
36-0	0.2973	3.33 (5.5)	3.00 (4.9)	- -	0.31 (0.4)	1.39 (2.0)	0.27 (0.5)	(13.4)	(28)	(8)
37-I	0.2246	11.57 (19.2)	10.83 (17.6)	2.00 (3.0)	1.75 (2.2)	2.85 (4.1)	1.05 (1.9)	(32.5)	(80)	(64)

[a] All concentrations in mg/m^3 of flue gas determined from elemental atomic absorption (carbon by IR-CO_2)
[b] See Table 3A
[c] Calculated stoichiometric amount of metal oxides
[d] Sum of the stoichiometric metal oxides plus carbon
[e] Gravimetrically determined insoluble particulate

Power Plant Metals Inventory

Based on the fuel oil ash analyses and the Liqui-Mag (MgO) additive rate, it was possible to calculate the expected furnace gas concentration of the principal metals as shown in Table 5. At the Northport Unit 3, the soluble and insoluble metal determinations were added together and averaged at both the inlet and outlet of the ESP as shown for the July and October 1977 runs.

For the July runs, a major fraction (71%) of the MgO was removed by the furnace system (as bottom ash and as fly ash tube deposits) since the Mg decreased from 65.2 to 18.6 mg/m^3. Of this latter amount entering the ESP, about 54% was removed (i.e., another 15% of the furnace MgO) even though the ESP was functioning only at 40% efficiency. Thus the total amount of the injected MgO retained in the unit was 87%. As stated earlier, Liqui-Mag (MgO) was added to the fuel primarily to inhibit high temperature wastage and low temperature corrosion, but, at Northport, also aided substantially in the recovery of generally over 80% of the salable vanadium from the oil (11).

Although the boiler portion of the system retained 72% of the Mg and the ESP another 15% (for a total of 87%), the boiler only retained 34% of the vanadium and the ESP another 39% for a total of 73% retained. In October, when the ESP was found to be much more efficient, the portion of Mg retained by the boiler was the same (70%), but that by the ESP climbed to 26% for a total of 96% retained in the unit; with respect to Mg, the ESP was 86% efficient. However, the vanadium retained by the boiler and ESP combined was not much higher than in July, primarily because the efficiency of the ESP with respect to vanadium was only 64%. This difference in ESP efficiency for Mg and V particulates, 86% and 64%, respectively, implied that the V particles must have been substantially smaller in size.

Further details on the distribution of the elements will be presented elsewhere (3a).

Table 5. Power Plant Metals Inventory

Power Plant	Flue Gas Region	Gas Concentration, mg/m^3					Efficiency Esp, %
		Mg	V	Na	Ni	Ca	
Northport (Unit 3) July 1977	Furnace[a]	65.2	24.4	9.4	3.2	1.15	
	ESP Inlet	18.6	16.0	5.7	2.6	1.1	
	ESP Outlet	8.6	6.5	2.8	1.1	1.2	
	(% Retained)	(87)	(73)	(70)	(66)	(0)	40
Northport (Unit 3) Oct. 1977	Furnace[a]	35.5	30.0	6.3	(3.2)	(1.2)	
	ESP Inlet	10.8	17.2	5.0	2.1	0.8	
	ESP Outlet	1.5	6.2	1.9	0.5	0.3	
	(% Retained)	(96)	(79)	(70)	(86)	(71)	73
Barrett (Unit 1) Aug. 1977	Furnace[a]	7.5	0.32	3.3	1.4	1.2	
	Stack	1.2	0.43	1.6	0.3	---	
	(% Retained)	(84)	(0)	(51)	(79)	---	none

[a] Furnace gas concentration of metals was calculated from oil ash analysis and MgO additive rate.

PARAMETERS AFFECTING SULFATE EMISSIONS

In the preceding sections, the principal variables affecting either sulfuric acid or sulfate formation and emission levels were shown to be

1.	Furnace O_2	H_2SO_4 (↑) and SO_4 (↑)
2.	ESP	SO_4 (↓) only
3.	Fly ash recirculation	H_2SO_4 (↓) and SO_4 (?)
4.	Sulfur in oil	H_2SO_4 (↑) and SO_4 (?)
5.	Vanadium in oil	H_2SO_4 (↑) and SO_4 (↑)
6.	Other metals in oil	H_2SO_4 (?) and SO_4 (↑)

For example, increasing furnace O_2 had direct effects on increasing sulfuric acid and metal sulfates. The electrostatic precipitator directly affected metal sulfates only; the higher the efficiency of the ESP, the lower the metal sulfate emissions. Indirectly, the ESP at Northport appeared to be responsible for a reduction in H_2SO_4 emission because of reduced catalytic activity of the recirculated fly ash. Increasing vanadium apparently had a direct effect on increasing catalytic activity and thus increasing H_2SO_4 and metal sulfates. The level of total metals in all probability controlled the level of total metal sulfates.

Some additional factors which were not yet investigated but are to be considered in upcoming measurements (3a) were the Liqui-Mag additive rate, the power level, and the burner tilt in the furnace.

Since increasing the MgO content would increase the total metal content in the flue gas, quite possibly the metal sulfates might increase. Counteracting that, however, would be the diluting effect of the MgO on the concentration of vanadium available for catalytic formation of H_2SO_4 and metal sulfates. Thus, the net effect of increasing MgO would probably be to reduce H_2SO_4 and metal sulfate emissions; such results have been noted by others (3b).

All else being equal, reducing power level, or load, has been shown to have a disproportionately higher reduction in total sulfate emission (10)(11). The precise effect on H_2SO_4 and metal sulfates will be assessed in future measurements.

Finally, reducing burner tilt has been shown to have a slight but perceptible decrease on total sulfate emissions (16). Again, there was no distinction made between sulfuric acid and metal sulfates.

COMPARATIVE STUDIES

Although there have been numerous studies conducted over the years on the magnitude of the emissions of metal sulfates and sulfuric acid from oil-fired power plants, there are two results of interest on the determination of metal sulfates that will be reported here for comparison with the Brookhaven measurements.

The EPA has been conducting studies (17) at several oil-fired power plants using the EPA Method 5 (18) for the determination of metal sulfates. Their results were plotted in Figure 10 as total metal sulfate concentration versus furnace oxygen as well as all the Brookhaven data for the Northport Unit 3 measurements at the ESP inlet and that obtained at Barrett. The Brookhaven results at Northport were in qualitative agreement with those determined by EPA at plants A1, A2, and W. Similarly, the Brookhaven results at Barrett were in excellent agreement with the EPA results at a very similar plant M.

The results depicted in Figure 10 confirm the existence of an intercept for particulate metal sulfate formation at zero furnace oxygen, i.e., in the absence of sulfuric acid. The figure also demonstrated the dependence of metal sulfates on furnace oxygen levels as well as the sulfur and vanadium content of the fuel. The magnitude of the metal sulfate level at Barrett and plant M was lower than that at the other plants because the fuel sulfur content was less. The dependence of the metal sulfate concentration on furnace oxygen level, that is, the slope of the line, was much less than the others because of the much lower vanadium content.

A study was performed by LILCO (19) at the Barrett Unit 2 about nine months prior to the Brookhaven measurements at Barrett Unit 1. LILCO found a total sulfate level of 1.9 ± 0.3 ppm, quite in line with the Brookhaven value of 2.5 ± 0.8 ppm, especially when consideration was given to the fact that Unit 1 had no operating particulate controls, but Unit 2 had an operating cyclone where all the collected particulates were re-injected back into the furnace. All other conditions were the same.

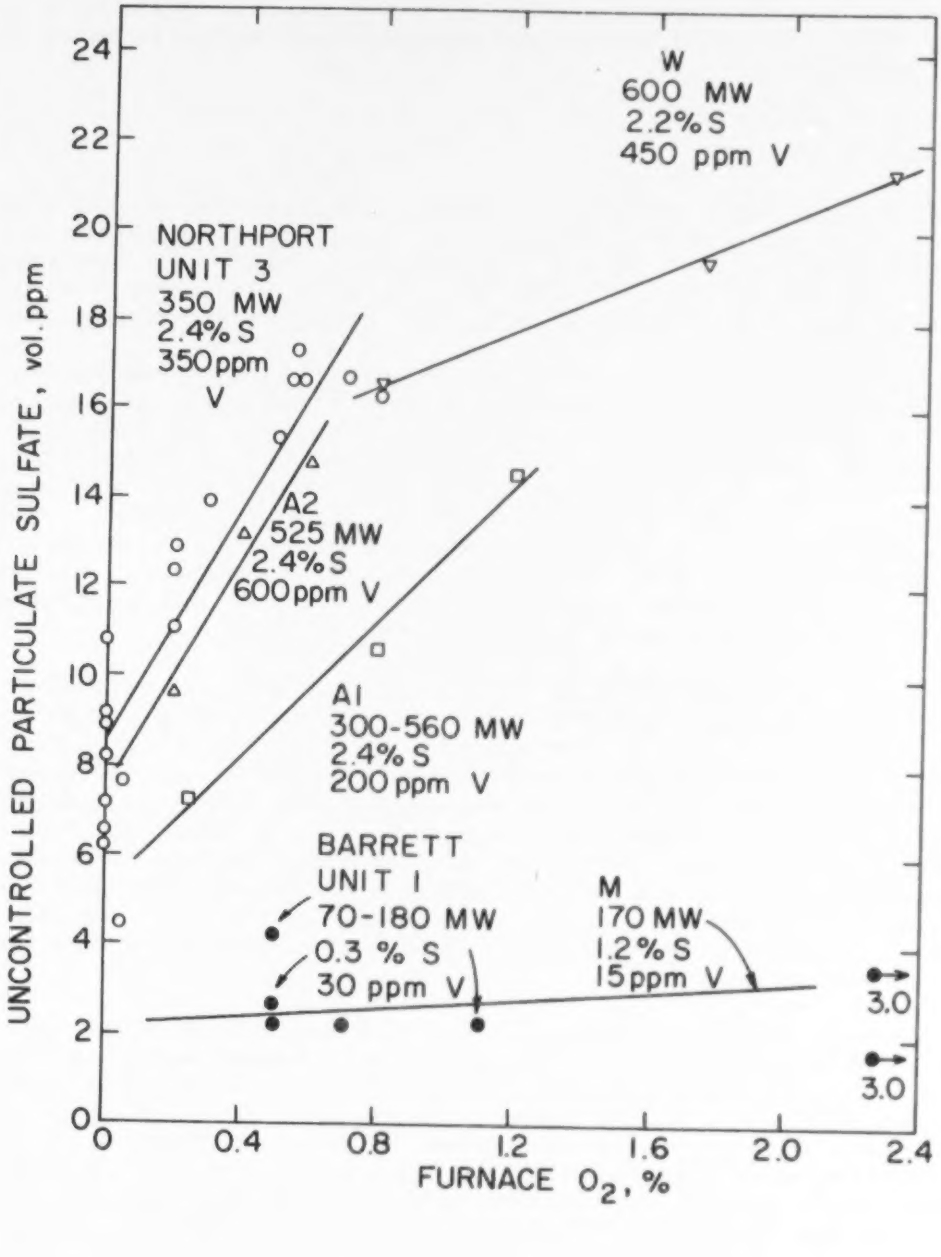

Figure 10. Effect of furnace oxygen and fuel oil sulfur and vanadium content on metal sulfate emissions at several oil-fired units.

CONCLUSIONS

The field utilization of the Brookhaven controlled condensation system at several oil-fired power plant units demonstrated the capability of a reasonably simple but quite reliable approach to the sampling of flue gas for the specific constituents, H_2SO_4 and total particulates; the latter were subsequently separated into a water-soluble and insoluble fraction. The soluble fraction was shown to be entirely composed of water soluble metal sulfates--principally of Mg, V, and Na. Carbon was the main element in the insoluble fraction which also contained metal oxides primarily of Mg, V, and iron.

Furthermore, it was conclusively shown that unless the flue gas sampling method used to study the effect of operating parameters on the emission of total sulfates was specific for H_2SO_4 and metal sulfates, the exact nature of the mechanisms responsible for the variability of sulfate emissions would have been more difficult to ascertain.

Those parameters shown to have the main effects on sulfuric acid emissions were furnace oxygen (H_2SO_4 increased with increased O_2), fly ash recirculation (H_2SO_4 decreased with recirculation), and the fuel oil sulfur and vanadium content (an increase in either constituent increased the H_2SO_4). Metal sulfates (MSO_4) were primarily governed by furnace oxygen (MSO_4 increased with increasing O_2 but to an extent proportional to the vanadium content of the fuel--i.e., with little or no vanadium in the fuel, MSO_4 was constant and independent of furnace O_2), the ESP (MSO_4 decreased with increasing precipitator efficiency), and the vanadium and other metal content of the fuel (MSO_4 increased with increasing vanadium and generally also with other metals).

From the results to date it appeared that there were two regions responsible for the formation of H_2SO_4 and metal sulfates. At one, the post-flame region, it is postulated that a portion of the flame-induced super-equilibrium SO_3 (3b) caused the formation of metal sulfates somewhat independent of furnace O_2 levels. Those metal sulfates corresponded to the intercept values in Figure 10. The other region, the superheater and reheater tubes of the boiler, was responsible for the catalytic formation of sulfuric acid with a concomitant amount of metal sulfates, dependent on the vanadium and furnace oxygen levels.

Finally, it was demonstrated that one direction that can be taken to reduce H_2SO_4 and metal sulfate emissions was to burn fuel oil containing low amounts of sulfur (<0.3% S) with little vanadium (<30 ppm V)--that is, the experience at Barrett. However, an equally acceptable and probably less expensive approach has been demonstrated at Northport Unit 3--a high sulfur (2.4%), high vanadium (350 ppm) oil-fired unit. By maintaining furnace oxygen at or below 0.1%, sulfuric acid was held to about 1 ppm, and by maintaining the ESP at 90% efficiency or better, metal sulfates were held to less than 2 ppm. Thus, at a properly controlled high sulfur, high vanadium oil-fired unit, the absolute emissions of total sulfates (~3 ppm) were held to the same level as at a low sulfur, low vanadium oil-fired unit (~2 ppm).

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Report of the Working Group on Characterization of Particulate Sulfur Oxides Emissions

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This Working Group had the objective of reviewing the status of characterization data for particulate sulfur oxides emissions. Its conclusions and recommendations are as follows.

STATUS AND VALIDITY OF AVAILABLE DATA

The group felt that the data presented during the workshop, while certainly very extensive, did not represent all that was known about particulate sulfur species. It further noted that additional information, especially that pertaining to emissions from coal combustion, was likely to be forthcoming from sources outside the United States, due to the greater length of time during which a number of countries (notably in Europe) have been utilizing coal as a fuel.

The foregoing statement notwithstanding, it was felt that sufficient data were available to provide considerable insight into both qualitative and quantitative aspects of the formation, transformation, and emission of particulate sulfur-containing species. In assessing the validity of these data the following points were noted:

1. Available sampling and measurement technology are quite adequate to describe the general behavior of primary sulfur oxide emissions and, in several cases, are sufficiently reliable to enable rather precise and accurate measurement of individual species.

    - Measurement methods for sulfur dioxide are quite adequate for present needs.

- Determination of particulate sulfate salts is also adequate, although it is noted that most of the available procedures only measure those sulfate salts which are readily soluble in water under specified conditions.
- Measurement methods for determining sulfur trioxide and sulfuric acid definitely need to be improved and at present probably only indicate lower limits of these species.
- At present, methods for the identification of individual metal sulfates are in their infancy and need to be improved.

2. Processes which result in the formation and transformation of particulate sulfur-containing species and which are known to occur both in combustion sources and in emitted plumes include:
    - Condensation of sulfur trioxide/sulfuric acid.
    - Adsorption of sulfur trioxide/sulfuric acid onto fly ash particles.
    - Chemical reaction of sulfur trioxide/sulfuric acid with chemical constituents of fly ash particles.
    - Direct interaction of sulfur dioxide with fly ash particles. While definitive information is sparse, it is probable that this also takes place.
3. The parameters which control the formation and subsequent emission of particulate sulfate salts are generally rather poorly defined; however, it is clear that the following factors undoubtedly influence these processes:
    - The temperature profiles within the combustion zone, stack system and plume.
    - The amount of oxygen present.
    - The characteristics of the fuel.

RECOMMENDATIONS

The group recognizes that particulate sulfur species generally account for only a minor fraction of the total primary sulfur oxides derived from conventional combustion processes. On the other hand, it is these particulate species which often play a controlling role in determining the environmental impact of emitted sulfur oxides. Consequently, the following recommendations are directed towards elucidation of the characteristics of combustion particulates and of the processes of formation of particulate sulfur oxides.

1. More detailed information is required concerning the condensation of vapor phase sulfur trioxide/sulfuric acid so that prediction of the temperature dependence of this process can be made more precise.
   - More precise definition of the controlling parameters, especially the role of nucleating particles, is required.
   - The size distribution of condensed droplets or particles must be established more precisely, and the factors controlling this size distribution must be identified.
2. Information is required concerning the rate, extent, and mechanism of formation of sulfate salts from sulfur trioxide and/or sulfuric acid.
   - The influence of the chemical composition of fly ash particles and the temperatures encountered must be established.
   - The particle size distribution of sulfate salts and the factors controlling this size distribution must be determined.
3. It is necessary to establish the relative importance of homogeneous and heterogeneous oxidation of sulfur dioxide to sulfur trioxide. In particular, there is a need to determine the role of fly ash particles in catalyzing this oxidation. In this regard it is noted that such catalysis may be due to one or more of the trace metal species associated with fly ash or to the presence of carbonaceous soot particles.

4. It is also necessary to establish the importance of direct sulfur dioxide-to-sulfate salt conversion. Relatively little is known about this potentially important pathway; however, it seems likely that its mechanism involves catalytic promotion, the nature and extent of which should be clearly established.

5. Studies of the physical and chemical characteristics of combustion particulates should be continued.

   - Compositional versus size characteristics should be firmly established.
   - Increased knowledge of the physical and chemical composition of particle surfaces should be sought.
   - Recognition should be given to the fact that the characteristics of emitted material may differ from those of material retained in particle control devices.

6. It is necessary to extend present studies of conventional combustion systems to emerging technologies involving fuel combustion or conversion and pollutant emission control. It is apparent that both the nature and amounts of sulfur emissions associated with several emerging processes differ significantly from those encountered in conventional combustion.

7. Finally, yet perhaps most important, it is recommended that an international working group or task force be established to gather information and establish a comprehensive data base dealing with primary sulfur oxide emissions from combustion sources. It is suggested that such a group be established through a United Nations Agency (e.g., WHO), since the problems addressed are of considerable international concern.

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